

THE PAINT LABORATORY NOTE BOOK

A Handy Guide to Works Practice

BY

JOHN STEWART REMINGTON



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Preface

THE notes in this book have been found very useful by the author when carrying out rapid tests on samples of pigments and paints submitted to him for analysis before conducting more exact quantitative tests. In typed form the notes have been given in the past on five or six occasions to friends in paint works, and have been much appreciated. So it is hoped that the information which has been brought together in this small handbook will be of use to paint manufacturers, especially the smaller firms who do not keep a qualified chemist, and who wish to make tests of the pigments and other raw materials they may be using.

A very modest outfit will enable anyone to carry out the tests herein described after a little practice, from the results of which valuable qualitative information can be obtained regarding the purity and quality of the goods being used for the manufacture of the various products.

J. S. R.

GARTHMEAD,
KINSBOURNE GREEN,
HARPENDEN, HERTS.

The Paint Laboratory Note Book

Preface to Second Edition

SINCE this book was published in 1935 several requests have been made to the author to incorporate quantitative methods not only as applied to the pigments mentioned, but as regards the general tests for oils, and more complete notes on volumetric analysis. Now a second edition has been called for this has been done, bearing in mind the importance of speed in the general routine work of a paint works laboratory. It is therefore hoped the book in its present enlarged form will be as well received by works chemists, especially the junior staff, as was the case when first published. I also wish to thank my friend Mr. E. A. Fishwick, Assoc.R.S.M., for the trouble he has taken in reading through the proof sheets, an undertaking he is well qualified to fulfil, having collaborated with me for some time. My thanks are also due to Miss M. N. Remington for reproducing all the illustrations in this book.

J. S. R.

GARTHEAD,
KINSBOURNE GREEN,
HARPENDEN, HERTS.

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THE PAINT LABORATORY NOTE BOOK

SECTION I

SIMPLE TESTS FOR WHITE

White Lead.—White lead consists of having the formula $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$. It is also known under the name of flake white, Kremnitz white and silver white. It is a heavy, white, amorphous powder with a specific gravity of about 6.65. Ground white lead is sold as genuine, and also in three reduced qualities—viz., No 1. containing 25 per cent. finest white barytes, No. 2 containing 50 per cent. barytes, and No. 3 grade 75 per cent. barytes.

White lead should conform to the following specification:

(I.) It must be pure basic carbonate of lead of soft texture and good colour.

(II.) It should contain between 25 and 33 per cent. of lead hydroxide, Pb(OH)_2 .

(III.) It should contain not more than 0.5 per cent. of moisture.

(IV.) It should contain not more than 0.5 per cent. of matters soluble in water.

(V.) On reducing 10 parts of white lead with 1 part of ultra blue, the resulting shade should be practically equal to that given by a standard genuine white lead treated in a similar manner.

(VI.) It should be quite soluble in nitric acid with evolution of carbon dioxide (CO_2).

The purity of white lead may be ascertained by dissolving 1 gram in a test-tube, in the cold, in dilute nitric acid; if the white lead is pure, it should be completely soluble in the acid—a residue indicating the presence of adulterants.

Any residue is usually barytes; but lead sulphate, china clay, gypsum, etc., have been found.

If a residue is found, place on a watch glass and moisten with hydrochloric acid. Dip a platinum wire in the mixture, and hold it at the base of the Bunsen flame; a green flame

(apple green) will indicate barium. Having filtered off the residue (barytes), treat the filtrate with sulphuretted hydrogen (H_2S); this will bring down all the lead as sulphide (PbS). Filter off the black sulphide, and to the filtrate, after boiling for about ten minutes to drive off excess sulphuretted hydrogen, add, when nearly cold, ammonia; a white precipitate would indicate alumina (china clay). Filter off the precipitate and test the filtrate with ammonium sulphide; a white precipitate will indicate zinc (ZnS). Zinc is not found as an adulterant of white lead, but may be present in one of the modern "combined pigments." The zinc sulphide is filtered off, and to the filtrate ammonium oxalate is added; a white precipitate will indicate calcium, pointing to adulteration with calcium carbonate (chalk) or calcium sulphate (gypsum). Such adulteration is, however, very unusual. The calcium can be confirmed by the flame test with platinum wire, imparting to the Bunsen flame a red colour of yellowish to orange shade.

White lead weighs about 180 lbs. to the cubic foot, and takes 7 to 12 per cent. of oil, or roughly 1 gallon per cwt. of white lead.

Basic lead carbonate	$2PbCO_3, Pb(OH)_2$
Specific gravity ..	6.335-6.750
Refractive index ..	1.94-2.09
Oil absorption ..	7-12 per cent.
Particle size ..	0.65-1.21 microns

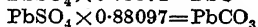
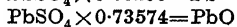
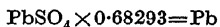
Quantitative Estimations.

Moisture.—Weigh out 10 grams of the sample into a tared dish and dry in the water oven to constant weight. The loss in weight multiplied by 10 gives the percentage of moisture.

Insoluble Matter.—Take 10 grams of the dry sample on which the moisture has been previously determined, and treat with dilute acetic acid and warm slightly. Filter off any insoluble matter. This may be silica or, in the case of a reduced white lead, barytes. Wash the residue well with boiling water and dilute acid, dry in oven, and ignite in a silica crucible. Should the residue be appreciable it should be treated with hydrofluoric acid in a platinum crucible, ignited and weighed. Should the residue be white it is most likely barytes, and can be identified by the flame test using a platinum wire dipped in the powder; flame apple green after the weight of residue has

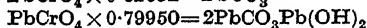
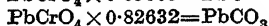
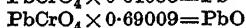
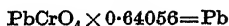
been recorded. Weight found $\times 10$ = percentage of insoluble matter.

Lead Estimation.—Dissolve 1 gram of the sample in a mixture of 15 c.c. glacial acetic acid and 15 c.c. water; heat until solution results. Then filter off any impurities (insoluble matter) and wash well with boiling water. To the filtrate containing the lead as acetate add 50 c.c. dilute H_2SO_4 (1 in 4) and evaporate until the acetic acid is driven off. Cool, dilute with 200 c.c. water, adding 5 c.c. alcohol, and allow to stand not less than four hours, and filter on to a weighed Gooch crucible charged with a plug of asbestos pulp, and wash with 1 per cent. sulphuric acid, then dry, ignite at a low heat, cool, and weigh as lead sulphate.



Bichromate Method for Lead.—Weigh out 0.5 gram of the sample into a 400 c.c. conical beaker and dissolve in 10 c.c. dilute acetic acid. Add about 5 grams of ammonium acetate, and dilute to about 150 c.c. with distilled water. Now bring up to the boil and add 10 c.c. saturated potassium bichromate solution. Continue to boil until the lead chromate formed has changed from a light yellow to almost a brick red. Allow the beaker to stand on the hot plate until the precipitate has settled. Filter off the precipitate through paper pulp and wash thoroughly with boiling water until the precipitate is quite free from soluble chromates. Dissolve the precipitate, using a special $NaCl + HCl$ solution, and also wash the paper pulp with the same solution; transfer the solution to the original beaker. The special solution is made by dissolving 550 grams $NaCl$ (Saxa salt) in 250 c.c. strong HCl , and making up 2,500 c.c. distilled water. Add a little of this salt solution if necessary to the beaker in order to complete the solution of the precipitate, and then add 3 grams of KI and a few c.c. of freshly prepared starch solution, and titrate at once with $N/10$ standard sodium thiosulphate which has been previously standardised against pure metallic lead or lead sulphate; on titration the end point will be reached when the blue colour due to the starch-iodine is just discharged. One c.c. of the $N/10$ sodium thiosulphate is equivalent to 0.0069 gram of lead.

The chromate method can also be carried out gravimetrically as follows: Having produced the lead chromate as before described, filter through a weighed Gooch crucible, being careful not to add any more of the precipitate than possible. Now add about 100 c.c. hot distilled water to the precipitate in the beaker and bring up to the boil, allow to settle, and decant as before, repeating these washings until the water is colourless; then transfer the precipitate to the crucible and wash with hot water. Finally, give two washings with dilute alcohol (50 : 50) and one wash with ether. Place the crucible in the hot water oven and dry at 105°C . for about thirty minutes, cool, and weigh as lead chromate, PbCrO_4 .



Carbon Dioxide.—The standard apparatus required for carrying out the determination of carbon dioxide in white lead is arranged as follows:

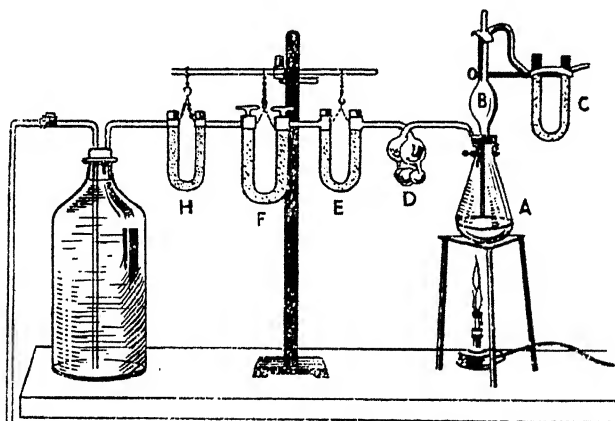


FIG. 1.—DETERMINATION OF CO_2 : (I) STANDARD METHOD.

One or two grams are weighed out and carefully transferred to the flask (A). To prevent any CO_2 entering the apparatus from the atmosphere the U-tube (C) attached to the acid

dropper (B) is charged with soda lime. The acid dropper can be conveniently made with a pipette or small separating funnel, and contains dilute hydrochloric acid. The glass bulbs (D) contain H_2SO_4 , the U-tube (E) contains copper sulphate pumice to prevent any hydrogen chloride passing, the U-tube with taps (F) contains soda lime to absorb the CO_2 , while the last U-tube (H) contains calcium chloride to prevent any water vapour coming back from the aspiration. Having fitted up the apparatus and made certain that there are no leaks, the U-tube F is carefully weighed and then replaced. The aspirator is disconnected at first, when the apparatus is started. The acid in the dropper is then allowed to flow on to the sample in the flask (A), which is gently heated. When all effervescence due to the escape of CO_2 has ceased, the aspirator is connected and air aspirated through the apparatus about ten times the capacity of the flask (A). The taps of the U-tube (F) are then closed, and the tube removed and allowed to rest for about half an hour till it has acquired the temperature of the air and is weighed, and from the increase in weight the CO_2 in the white lead can be calculated.

$$\frac{\text{Increase in weight of U-tube (F)} \times 100}{1} = \text{CO}_2 \text{ per cent.}$$

The carbon dioxide in white lead may vary, and usually will be found to be anything from 11.24 to 12.30 per cent.

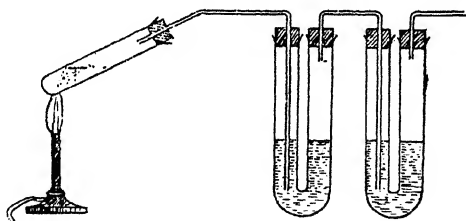


FIG. 2.—DETERMINATION OF CO_2 : (II) QUICK WORKS LABORATORY METHOD.

For general works purposes a more simple apparatus can be used (F. L. Jameson, *Paint Manufacture*, November, 1938). When using this apparatus a small portion of the sample is weighed out and transferred to a dry test-tube and the CO_2

and combined water collected in two U-tubes which have been previously weighed, the first containing H_2SO_4 and the second KOH. The increase in weight of the first U-tube will give the combined water and the increase in weight of the latter tube the CO_2 , and assuming the white lead is pure, the residue in the test-tube will be lead oxide (PbO).

Detection of Water in Pulp White Lead.—Take some of the paste and rub it up on a glass slab with a small quantity of dry eosine. If water is present, a pink colour will be produced due to the formation of red ink. Eosine is insoluble in oils, turpentine and white spirit.

Lead Sulphate.—This pigment is also known as non-poisonous white lead or Freeman's white lead (PbSO_4). It is a white crystalline body, whiter than genuine white lead, and practically insoluble in water, and insoluble in alcohol. It is not used as a pigment, but finds an extended use for mixing with lead chromes. The amount of oil required when grinding is higher than white lead, being about 10 per cent. Specific gravity, 6.082.

Lead sulphate is soluble in hot concentrated nitric acid or hydrochloric acid; also in ammonium acetate, citrate and tartrate. In the case of the citrate and tartrate, the solution should be strongly alkaline with ammonia. Lead sulphate is also very soluble in hot solutions of potassium or sodium hydrate.

Sublimed White Lead (Basic Lead Sulphate).—This class of white lead is extensively manufactured in America from mixed ore consisting of galena (lead sulphide) and zinc blende (zinc sulphide). These leads when mixed with linseed oil form a paint which retains its gloss and is proof against excessive "chalking." Specific gravity, 6.396.

The chemical composition is approximately $\text{PbO} \cdot 2\text{PbSO}_4$. It is practically insoluble in dilute acids, and not easily acted on by sulphuretted hydrogen. It dissolves in boiling hydrochloric acid, the solution on cooling depositing white lead chloride. Take some of the deposit and shake up with distilled water in a test-tube; now add a few drops of potassium iodide; a yellow precipitate will form (PbI_2); filter, if necessary; some of the iodide will dissolve, and be re-formed on cooling.

The following are analyses of sublimed white lead:

SIMPLE TESTS FOR WHITE PIGMENTS

	I.	II.	III.
Lead sulphate	70.00	75.02	75.20
Lead oxide ..	23.00	18.48	19.32
Zinc oxide ..	7.00	6.22	5.40
Combined water	—	—	—
Moisture ..	—	—	0.08
Silica	—	0.28	—
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00
Formula	$\text{PbSO}_4 \cdot \text{PbO}$	
Specific gravity	..	6.396-6.41	
Refractive index	..	1.93	
Oil absorption	..	10-11 per cent.	
Particle size	..	0.65-0.67 micron.	

Quantitative Estimations.

Moisture as described under white lead.

Insoluble Matter and Total Lead.—Take 1 gram of the sample, place in a 250 c.c. beaker and damp with a few drops of alcohol, and add 50 c.c. of a saturated solution of ammonium acetate. Heat to boiling for two minutes. Filter off, leaving any insoluble in the beaker. To the residue in the beaker add 50 c.c. acid ammonium acetate solution and boil for about two minutes.

Filter off through the same filter paper previously used and wash with boiling water, and dry the residue in an oven; ignite and weigh as insoluble matter in the same manner as previously described for white lead.

Unite the acid ammonium acetate solutions, heat to boiling, and add 10 to 15 c.c. of a 10 per cent. solution of potassium dichromate. Heat up until the yellow precipitate turns an orange-red colour, settle on the hot plate, and then proceed to determine the lead as previously described under white lead, either gravimetrically or volumetrically, in the latter case titrating with N/10 sodium thiosulphate.

Zinc Oxide.—Weigh out 1 gram of the sample and place in a 500 c.c. beaker, and add 30 c.c. HCl (1 in 2); boil for about five minutes, add 200 c.c. distilled water, put in a small piece of red litmus paper, and add NH_4OH to slight alkalinity.

Now acidify with HCl, adding 5 c.c. in excess, heat to boiling, and titrate with potassium ferrocyanide, calculating the zinc to ZnO , as described under Zinc Oxide.

Lead Sulphate.—Take 0.5 gram of the sample, place in a 500 c.c. beaker, damp with a few drops of alcohol, add 10 c.c. bromine water, 10 c.c. HCl (1 in 1), and 3 or 4 grams of NH_4Cl . Cover the beaker with a watch glass and heat on a steam bath for about five minutes. Now add boiling water, making the whole up to about 200 c.c., and boil for five to ten minutes, filtering off any insoluble matter, and wash with hot water. Neutralise the filtrate with solid Na_2CO_3 , and then add an extra gram of the sodium carbonate and again boil for twelve minutes, or if necessary slightly longer. Be careful to wash the cover glass, allow to settle, filter, and wash with hot water.

Redissolve the precipitate in HCl (1 in 1) and again reprecipitate with Na_2CO_3 , again filter, and wash with boiling water ten times. Now acidify the united filtrates with HCl, being sure you make the filtrate slightly acid. Boil up to expel the last traces of bromine, and while the solution is boiling add 15 c.c. of a 10 per cent. solution of barium chloride; allow to stand on the hot plate for about thirty minutes, filter into a weighed Gooch crucible charged with a previously ignited asbestos pulp plug. Wash ten times with boiling water, dry, ignite, cool, and weigh the BaSO_4 , and calculate to PbSO_4 . $\text{BaSO}_4 \times 1.29769 = \text{PbSO}_4$.

To express the results, calculate the PbSO_4 to PbO by using the factor 0.736, and subtract this from the percentage of PbO found under Total Lead and report the difference as PbO.

Zinc Oxide.—This pigment is also known as 'zinc white, Chinese white, and Hubbuck's white. Zinc oxide is a soft, tasteless, and odourless white powder, having a specific gravity of 5.554 to 5.60, and requires 12 to 23 per cent. of oil to grind it into paste form. It is quite permanent, and is not darkened on exposure to fumes of sulphuretted hydrogen (H_2S). On gently heating it turns yellow, but regains the white condition on cooling.

Zinc oxide is insoluble in water, alcohol, linseed oil, turpentine, and benzine. It is readily soluble in dilute acetic, nitric, hydrochloric, and sulphuric acids. Zinc oxide is soluble in hot alkaline solutions of the fixed alkalies, but not in their carbonates.

The presence of chlorides in zinc oxide can be detected by

dissolving a small portion in dilute nitric acid and adding a few drops of silver nitrate, when a white precipitate of silver chloride will indicate chlorides, if present.

Sulphates may be detected by dissolving a small portion in dilute hydrochloric acid, boiling well, and adding boiling barium chloride. If sulphates are present, a white precipitate will be produced. Zinc oxide should be completely soluble in dilute sulphuric acid (1 in 5) without effervescence. Should effervescence occur, this is due to natural absorption and combination with carbon dioxide from the atmosphere in conjunction with combined moisture. The presence of lead in zinc oxide can be detected by making up the oxide with refined linseed oil into paste and spotting the paste with a drop of ammonium sulphide. The greater the amount of lead present the darker the stain.

A practical test for the presence of zinc oxide in any compound or pigment may be carried out in the following manner:

Boil in a beaker about 1 gram of the substance to be tested with 30 c.c. dilute sulphuric acid (1 in 5) for fifteen or twenty minutes and allow to settle; if a residue appears, filter off, and keep the clear filtrate. Divide the filtrate into two parts; dilute one with an equal volume of water, and make the other distinctly alkaline with ammonia. To the acid filtrate add potassium ferrocyanide solution; a gelatinous precipitate of a pale bluish-green colour will indicate zinc. To the alkaline solution add ammonium sulphide; a white feathery precipitate of zinc sulphide will be formed, if zinc is present. It is not often that adulterants such as calcium carbonate (chalk) or calcium sulphate (gypsum, terra alba) are found, but, if present, they would be detected as follows:

Treat with dilute hydrochloric acid; a strong effervescence would indicate chalk (CaCO_3). For the detection of gypsum, the sample of the zinc oxide is boiled with distilled water, calcium sulphate being slightly soluble in boiling water; filter, add ammonium hydrate, and then ammonium oxalate to the filtrate. Should gypsum have been intentionally added, a white precipitate of calcium oxalate would be formed. Confirm, having previously filtered off the precipitate, by platinum wire in Bunsen flame. Flame for calcium, reddish-yellow to orange.

Formula	ZnO (Zn 80.34, O 19.66)
Specific gravity	5.47-5.554
Refractive index	2.02
Oil absorption (B.E.S.A.) .	12-29
Particle size:	
Fine cosmetic (French) .	0.12-0.18 micron.
Indirect or French oxides .	0.2-0.35 ..
Direct or American process	0.28-0.35 ..

Quantitative Estimations.

Moisture.—Ten grams of the sample are weighed into a shallow dish which has been previously heated, cooled, and weighed.

The sample is then placed in a drying oven and maintained at 105° C. for two hours; then taken out, cooled, and weighed.

The dish is then replaced in the oven for half an hour, again cooled in the desiccator and weighed. The loss in weight represents hygroscopic moisture, and this loss in weight multiplied by 10 gives the percentage.

Loss on Ignition.—Two grams of the sample which have been dried at 105° C. are placed in a previously cooled and weighed silica dish. The sample is then placed in a muffle, and raised to a temperature of approximately 500° C. for fifteen minutes; then taken out, placed in the desiccator, cooled and weighed. The dish is again heated, and if the loss in weight is constant, the figure is taken as loss on ignition (CO₂ + combined moisture).

$$\frac{\text{Loss in weight} \times 100}{2} = \text{loss on ignition.}$$

Determination of Soluble Salts.—According to the British Engineering Standards Specification for Zinc Oxide, Bulletin No. 239, the amount of matter soluble in water for type I Zinc oxide—that is, an oxide of 99 per cent. ZnO—must not exceed 0.25 per cent., while an oxide of type II—that is, an oxide containing 96 per cent. ZnO—must not exceed 0.40 per cent. The determination of the soluble salts is carried out as follows: Weigh out 5 grams of the sample, place in a dry beaker and damp with ethyl alcohol about 2 to 4 c.c., then add 200 c.c. distilled water, and boil for five minutes. Cool to room temperature and transfer to a 250 c.c. flask, and make up to 250 c.c. with distilled water, shake well, and filter. Reject the first 100 c.c. of the filtrate, and then take 100 c.c. and evaporate to

dryness in a previously weighed and cooled platinum or silica dish on a water bath. When evaporated, dry the residue to constant weight in an air oven at 105° .

$$\frac{\text{Dish} + \text{residue} - \text{dish} \times 100}{2} = \text{percentage of matter soluble in water.}$$

Insoluble Matter.—Twenty-five grams of the sample are taken and placed in a 250 c.c. beaker, 50 c.c. of water and 50 c.c. HCl are added, and the whole evaporated to dryness. The residue is then taken up with 50 c.c. dilute HCl (1 in 4), filtered off and thoroughly washed with 1 in 4 HCl and then with boiling water, followed by ammonium acetate solution, and finally again with boiling water. The residue is then dried, burnt off, and weighed in a previously weighed silica or platinum crucible and the residue expressed as SiO_2 .

Sample taken 25 grams.

Weight of residue 0.007.

$$0.007 \times 4 = 0.028 \text{ per cent. } \text{SiO}_2.$$

Chlorine and Chlorides.—This determination is carried out by the use of standard silver nitrate and by using either potassium sulphocyanide (KCNS) or ammonium sulphocyanide (NH_4CNS).

This method depends upon completely precipitating the chlorine in the presence of nitric acid by a measured excess of standard silver nitrate solution, and then determining the excess of silver nitrate by retitrating with standard sulphocyanide, using as an indicator iron alum. The sulphocyanide, having a greater affinity for the silver than it has for the ferric iron, reacts with the silver nitrate first, but as soon as this is satisfied, the sulphocyanide will combine with the ferric iron and cause a brownish-red colour to make its appearance.

The sulphocyanide solution must be made of such a strength that it corresponds with the silver nitrate solution volume for volume.

Standard Silver Nitrate: 4.799 grams per 1,000 c.c.

Standard Ammonium Sulphocyanide: 2.300 grams per 1,000 c.c.

AgNO_3 Solution: 1 c.c. = 0.001 gram Cl_2 .

The ammonium sulphocyanide is made up rather stronger than the silver nitrate, and diluted until the exact match is obtained.

Assuming 10 c.c. of AgNO_3 require 9.8 c.c. for neutralisation, if the residual volume is 983 c.c., then $\frac{9.8}{10} = \frac{983}{x}$, when x is the diluted volume. Calculate this volume, dilute, mix well and check up again. To carry out this chlorine estimation take 2 to 10 grams of the sample and add 25 c.c. of distilled water. To this is added 40 c.c. of HNO_3 and the solution boiled until nitrous fumes are removed. The solution is then cooled, 20 c.c. standard silver nitrate solution and 5 c.c. of a 10 per cent. solution of iron alum ($\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2 \text{SO}_4 + 24\text{H}_2\text{O}$) added, and the excess silver nitrate solution titrated with standard ammonium sulphocyanide to a faint pink, the colour being due to the formation of ferric sulphocyanide. Silver nitrate 1 c.c. = 0.001 gram Cl_2 .

Detecting Metallic Particles in Zinc Oxide.—Ten grams of the sample are mixed in a mortar with 0.1 gram anthraquinone and 20 c.c. of a 20 per cent. solution of NaOH and thoroughly ground. The paste is then transferred to a silica dish and gently heated. The development of pink spots indicates the presence of metallic zinc particles.

Today in the rubber industry zinc oxides used in the rubber mix are sometimes coated with a monomolecular layer of fatty acid, such as stearic acid. To detect this take 10 grams of the sample and place in a small round-bottomed flask, and add 70 c.c. absolute alcohol, having connected the flask with a reflux condenser. Boil for thirty minutes, allow to cool, and wash out the sample with alcohol into a porcelain basin, add a few drops of phenolphthalein and titrate with $\text{N}/10$ KOH . 1 c.c. = 0.0284 gram stearic acid.

Determination of SO_3 .—0.5 to 10 grams of the sample are dissolved in 15 to 30 c.c. of HCl , having previously added 150 to 200 c.c. distilled water. Bring up to the boil and add 10 per cent. BaCl_2 solution. Boil for a few minutes and then transfer to the hot plate, keeping the solution at about 98° to 100° C. for one hour or until the precipitate has completely settled.

Now filter through a double 30 Whatman filter paper, wash once with cold water, then with dilute HCl , once again with cold water, and then ten times with boiling water, after which the fresh filtrate collected in a test-tube should give practically no opalescence with a few drops of AgNO_3 .

Dry the precipitate in hot air oven, ignite in platinum or silica crucible (previously ignited, cooled and weighed) and weigh as BaSO_4 .

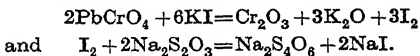
$$\frac{\text{Weight of ppt.} \times 0.3433}{\text{Divided by weight taken}} = \text{SO}_3 \text{ per cent.}$$

Estimation of Lead.—Bichromate method for oxides low in lead. Take 20 to 50 grams of the sample and dissolve in 250 to 300 c.c. of distilled water and 40 to 82 c.c. glacial acetic acid. Bring up to the boil. In the case of any direct oxide being treated the amount of sample taken is only 5 grams, and when adding the acetic acid a little solid ammonium acetate is also added.

Now add 10 c.c. saturated solution of potassium bichromate and boil for ten minutes, or until the precipitate coagulates and the yellow precipitate has turned to a brick red in colour, allow to stand on the hot plate for about thirty minutes, then filter through a Gooch crucible charged with paper pulp made from 31 Whatman filter paper and wash well with hot water.

Reject the filtrate from the filter flask, having washed away all traces of bichromate. Dissolve the precipitate by washing with acid sodium chloride solution (see preparation below) and wash with cold water, allowing the solution to run into the clean filter flask; now transfer the solution to a beaker. The amount of solution should be approximately 50 c.c.; add 3 grams of KI and titrate the liberated iodine with standard N/20 sodium thiosulphate solution, using starch solution as indicator, titrating to a colourless or bright yellow solution. A N/20 sodium thiosulphate solution contains 13.260 grams per litre (1,000 c.c.). 1 c.c.=0.004 gram PbO.

The reactions are:



The acidulated salt solution is made up as follows:

Table salt	550 grams.
Hydrochloric acid	250 c.c.
Distilled water	2,000 c.c.

Estimation of Lead by Molybdate.—From 10 to 50 grams of the sample are dissolved in hydrochloric acid and fumed with H_2SO_4 . When cool, the residue is taken up with water, boiled

for at least ten minutes and allowed to settle over night. The lead is then filtered off, using a Gooch crucible and paper pulp, the precipitate treated with ammonium acetate solution and the solution again filtered. The solution is then brought to the boil and 10 c.c. of a 10 per cent. solution of ammonium molybdate added. The precipitate is allowed to settle, filtered, dried, ignited and weighed. One gram of lead, molybdate contains 0.564 gram of lead (Pb).

Determination of Cadmium.—According to the grade of oxide to be examined take 5 to 25 grams and place in a 300 c.c. beaker and boil with 100 to 200 c.c. 1.5 per cent. H_2SO_4 ; then filter through a double 15 cm. English filter paper and wash six times with boiling water. Acidify the filtrate with H_2SO_4 , adjusting the acidity to 3 per cent. free acid, and pass H_2S until all the cadmium has been precipitated as yellow cadmium sulphide. Allow the precipitate to settle. Filter through paper pulp previously placed in a Gooch crucible and wash with cold water. Dissolve the precipitate with HCl and bromine water, collecting the solution in a 250 c.c. beaker. Evaporate down on the hot plate with a few drops H_2SO_4 to small bulk, and then transfer to a weighed silica dish and take down to dryness, being careful to drive off excess of H_2SO_4 . Heat in a low temperature muffle, cool, and weigh as CdSO_4 .

$$\frac{\text{Ppt} + \text{dish} - \text{dish} \times 0.5384}{\text{Divided by weight taken}} = \text{Cd per cent.}$$

or 0.6154 for CdO .

Estimation of Iron as Ferric Oxide (Fe_2O_3).—Take 25 grams of the oxide and dissolve in dilute HCl . Filter off the residue, if any. Now boil and add 10 grams of ammonium chloride and then ammonium hydrate, which will precipitate the iron as hydroxide. Boil well, place on the hot plate and allow the precipitate to settle, then filter. Redissolve the precipitate in as little HCl as possible and reprecipitate with ammonium hydrate. Filter, wash well with hot water and dry in oven. Place the dry precipitate in a weighed platinum or silica crucible, ignite the filter paper, adding the ash to the precipitate in the crucible and ignite over strong Bunsen flame, then cool and weigh. 25 grams taken weight of precipitate 0.0088.

$$0.0088 \times 4 = 0.035 \text{ Fe}_2\text{O}_3 \text{ per cent.}$$

Another Method.—Proceed as in the former method until the precipitation of the ferric hydroxide is complete, filter, and then wash back the precipitate into a flask fitted with a well-fitting rubber stopper and Bunsen valve.

Add 10 c.c. H_2SO_4 and 3 grams of pure zinc and allow the reduction to proceed preferably over night. When all the zinc has dissolved, titrate with N/10 potassium permanganate to a faint pink.

1 c.c. = 0.005585 Fe.

1 c.c. = 0.00798 Fe_2O_3 .

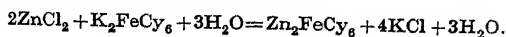
Estimation of Iron in Small Quantities.—From 50 to 100 grams of the sample are taken and dissolved in HCl, water added and oxidised with a few drops of HNO_3 and precipitated with NH_4OH . The iron hydrate is filtered off, dissolved in a small amount of HCl, and again precipitated with NH_4OH and well washed. The precipitate should now be clear and free from zinc, and is dissolved in a minimum quantity of HCl in 150 c.c. beaker oxidised with HNO_3 , 1 drop of H_2SO_4 added, and the beaker and contents allowed to go slowly to dryness on hot plate. When nearly dry (just moist) the contents are taken up with water and filtered into a Nessler glass (50 c.c.) containing 5 c.c. of a 20 per cent. solution of potassium sulphocyanide. The colour is then matched by using another Nessler glass containing a standard iron solution made by taking 0.7 ferrous ammonium sulphate ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) solution, oxidising with HNO_3 , fuming with 1 drop of sulphuric acid and making up to 1,000 c.c.; 1 c.c. of this solution will contain 0.0001 Fe. This should be diluted five times to give a working solution for matching 0.00002 Fe. This is an excellent method for small quantities of iron. Having determined the various minute impurities, it is the practice to take the zinc oxide by difference and to make up to 100 per cent., but should it be desired to estimate the zinc, it can be determined by one of the three following methods.

Estimation of Zinc as Pyrophosphate.—Dissolve 1 gram of the sample in 250 c.c. of water and 25 c.c. of glacial acetic acid. As soon as all the sample has dissolved add 5 c.c. H_2SO_4 and evaporate carefully to fumes of sulphuric anhydride. Now cool and dilute with 30 c.c. of water, filter through a Gooch crucible charged with previously ignited asbestos pulp, wash with 2 per cent. H_2SO_4 . The filtrate contains the zinc

as zinc sulphate. This is evaporated to about 100 c.c. and then cooled. As soon as the filtrate is cool, add 5 grams of hydrogen sodium ammonium phosphate ($\text{NaNH}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$) dissolved in 30 c.c. of cold water, stir well, and then add drop by drop ammonia to the neutral point. Now add 2 drops of ammonia and 1 c.c. acetic acid, stirring well, and then heat on the hot plate for an hour. The white precipitate will form with a crystalline structure, and settle down to an easily filterable product. The precipitate is then filtered through a Gooch silica crucible with an asbestos pad, and well washed with hot water, then dried in the water oven, and finally ignited at first at a very low heat in the muffle, and lastly to low redness. Then cool, and weigh as zinc pyrophosphate ($\text{Zn}_2\text{P}_2\text{O}_7$). Calculate to zinc oxide by multiplying by the factor $0.53409 = \text{ZnO}$ or by the factor 0.42911 for Zn. This is a very reliable gravimetric method for zinc.

Estimation of Zinc by Potassium Ferrocyanide.—Heat 1 gram of the sample in dilute HCl and when dissolved, should there be any residue, filter off. Remove lead and iron, and to the filtrate add water, making up to 250 c.c. in a graduated flask. Pipette out 50 c.c. into a beaker, acidify with HCl adding 5 c.c. in excess, boil, and immediately titrate with a standard solution of potassium ferrocyanide, using a 5 per cent. solution of uranium nitrate on a porcelain spot plate as indicator, to a slight brown tinge.

The potassium ferrocyanide is standardised as follows: Weigh out 0.2 gram of pure zinc, and dissolve in HCl (1 in 2) in a 500 c.c. beaker. Dilute and make alkaline with ammonia, again acidify with HCl, adding an excess of 5 c.c., dilute to 300 c.c., and boil. Now take 200 c.c., reserving 100 c.c., and titrate with the potassium ferrocyanide solution containing 21.55 grams of the salt per litre, running in a few drops at a time, until a drop tested on a porcelain tile which has been previously spotted with uranium nitrate solution gives a brown coloration. Now add the remaining 100 c.c. of zinc solution and titrate with great care until the end point is reached, which must be done by adding the ferrocyanide solution a drop at a time. If correctly carried out, 1 c.c. of standard ferrocyanide solution should be equal to 0.005 gram of zinc or 0.006 gram of zinc oxide. The reaction is as follows:



Determination of Zinc by Anthranilic Acid or O-Amino-Benzoic Acid.—Prepare a 5 per cent. solution of anthranilic acid as follows: Take 22 c.c. N/1 NaOH, 3 grams of anthranilic acid, and stir with a glass rod till dissolved, then filter and dilute to 1,000 c.c. Weigh out 1 gram of the zinc oxide, and dissolve in dilute HCl and make up to 1,000 c.c. Take 100 c.c. (0.1 Zn), add sodium carbonate solution to opalescence, then clear with 2 to 3 drops of acetic acid. Now add 30 c.c. of the anthranilic acid solution in the cold, and allow the precipitate to form, standing twenty minutes, stirring occasionally. Filter on to a weighed Gooch crucible charged with a plug of paper pulp and wash six times with water made up as follows: The above standard solution diluted ten to fifteen times with distilled water, and finished with three washes of dilute alcohol (50 in 50), then dry in an oven at 100° to 105° C., cool and weigh. This is a very excellent method, and rapid in working. On adding the standard anthranilic acid to the zinc solution a heavy finely crystalline and easily filterable precipitate of zinc anthranilate will come down.

$$\text{Ppt} \times 0.1937 = \text{Zn.}$$

Comparing the above three methods on a red seal zinc oxide, the following results were obtained:

	<i>Per Cent.</i>			
Ferrocyanide method	Zn 98.650
Pyrophosphate method	Zn 98.642
Anthranilic acid method	Zn 98.637

B.P. Test for Arsenic in Zinc Oxide.—The only oxides usually tested for arsenic are those to be used for pharmaceutical and cosmetic purposes, and these tests are carried out as follows: 5 grams of the sample are weighed out and placed in a special test bottle or flask together with two or three pieces of granulated zinc; a similar quantity of arsenic-free granulated zinc is placed in a similar flask to act as a blank. Standards are prepared by placing similar quantities of arsenic-free zinc in other flasks, and adding portions of the standard arsenic solution of which 1 c.c.=1 part per 1,000,000 on 5 grams of zinc oxide, 2 c.c.=2 parts per 1,000,000, and so on.

Now add about 15 c.c. water, and fix the mercuric chloride papers in position; also, to make sure there is no H₂S present,

have a wad of cotton-wool plus lead acetate solution which has been dried before being placed in position in the stem of the exit tube.

Fifteen c.c. of pure HCl is now added to each bottle, and the corks and tubes at once placed in position. Allow the action to proceed for about thirty-five minutes, when the stains on the mercuric chloride papers can be removed and examined. The mercuric chloride papers are made by soaking filter paper in HgCl_2 solution, and then drying for fifteen to twenty minutes in the hot-water oven, after which they are cut up into convenient pieces for use.

Leaded Zinc Oxides.—This pigment is a zinc oxide and lead sulphate combination, and various grades are made containing 5, 15, and 35 per cent. basic lead sulphate respectively. This pigment is not a mechanical mixture; the zinc and lead are in the nature of an alloy, being united by a process of sublimation. Leaded zinc oxides are pigments of small particle size of a white colour—not so white as pure zinc oxide, but about the same as white lead. The specific gravity varies from 5.52 to 5.95, and the oil absorption from 11.5 to 19.5 per cent.

Dissolve 1 gram by boiling in dilute nitric acid. To this add 5 c.c. of concentrated sulphuric acid and a few drops of absolute alcohol; allow to stand. White lead sulphate will come down. Filter off; to the filtrate add ammonia; then make acid with hydrochloric acid, and add potassium ferrocyanide solution; a bluish-white precipitate of zinc ferrocyanide ($\text{Zn}_2\text{Fe}(\text{CN})_6$) will be produced.

					<i>Specific Gravity.</i>
Leaded zinc oxide (5 per cent.)	5.70
" " " (35 " ")	5.95
Oil absorption (5 per cent.)	15.3
" " (15 " ")	14.8
" " (25 " ")	13.2
" " (35 " ")	12.1
Particle size	0.35-0.45 micron.

Quantitative Estimations.

Moisture.—Determined as for zinc oxide.

Lead.—Take 0.25 gram of the sample and dissolve in 50 c.c. nitric acid and 50 c.c. water. Dilute to 200 c.c. and filter if necessary. Boil down on the hot plate nearly to dryness and allow to cool, and add 10 c.c. H_2SO_4 . Mix well, and allow to

stand on the hot plate until sulphur trioxide fumes are seen to be coming off. Take off the hot plate and cool. Now add 40 c.c. distilled water and boil. Allow the lead sulphate to stand over night, and to insure the complete precipitation of the lead add 10 c.c. alcohol. Finally filter through a weighed Gooch crucible charged with asbestos pulp, dry, cool and weigh.

					Gram.
Quantity of sample taken	0.25
Weight of precipitate	0.100

$$0.100 \times 0.736 \times 4 = 2.944 \text{ PbO}$$

Soluble Sulphates.—Take 2 grams of the sample and place in a 250 c.c. beaker, and add 150 c.c. distilled water and 5 c.c. absolute alcohol and boil for ten minutes. Then allow to settle, filter and wash with dilute alcohol (1 in 3), reserving the filtrate. Boil the filtrate to expel the alcohol, then carefully add boiling barium chloride solution and continue boiling for about six minutes, then allow the barium sulphate to settle. Filter off through a Gooch silica crucible which has been previously dried and weighed and charged with an asbestos pad. Wash the precipitate ten times with boiling water, dry, ignite, cool and weigh the barium sulphate, and calculate to SO_3 and also to zinc sulphate.

$$\text{BaSO}_4 \times 0.34293 = \text{SO}_3.$$

$$\text{BaSO}_4 \times 0.69159 = \text{zinc sulphate.}$$

Total Sulphates.—Two grams of the sample are weighed and placed in a 600 c.c. beaker. To this are added 5 grams of powdered ammonium chloride and 15 c.c. water, and gently heated until the NH_4Cl has dissolved; 15 c.c. of HCl are then added, and the beaker, having been covered with a clock glass, is gently heated for five minutes until the zinc and lead have gone into solution. Now dilute to about 400 c.c. with hot water and boil for five minutes, filter while hot, and if there is any insoluble matter on the filter wash this with hot water, dry and ignite the filter paper and insoluble, cool in the desiccator, and weigh the insoluble matter.

If the sample is adulterated with barytes, test the insoluble residue by the flame test. Barytes gives a flame, colour green,

shade yellowish. If the result of the flame test is negative and only a very small amount of insoluble matter is present, express as silica (SiO_2). Take the filtrate, heat to boiling, and add 20 c.c. of barium chloride solution 10 per cent. strength. Allow this to stand on the hot plate for an hour until the white precipitate of barium sulphate has completely settled, then filter into a previously dried and weighed Gooch silica crucible and wash with boiling water. Then dry the precipitate in the oven, ignite, cool and weigh as barium sulphate:

$$\frac{\text{BaSO}_4 \times 0.343}{\text{Weight taken}} = \text{SO}_3 \text{ (total sulphates).}$$

Having thus obtained the soluble sulphates and total sulphates in conjunction with the total lead sulphate (PbSO_4), calculate as follows:

$$\text{Per cent. PbSO}_4 = \frac{(\text{total SO}_3 \text{ per cent.} - \text{per cent.})}{80} \times 303$$

$$\text{Per cent. PbO} = \frac{223}{207} \text{ total lead} - \frac{(\text{total SO}_3 - \text{soluble SO}_3)}{80} \times 207$$

or one can multiply the barium sulphate by 0.69195, which will give the equivalent of zinc sulphate, and from the total zinc sulphate thus obtained deduct the soluble zinc sulphate previously estimated and multiply the remainder by 1.87638, which will give the amount of lead sulphate in the sample.

The following factors may be found useful:

$$\begin{aligned} \text{BaSO}_4 \times 0.69159 &= \text{ZnSO}_4. \\ \text{BaSO}_4 \times 1.29769 &= \text{PbSO}_4. \\ \text{BaSO}_4 \times 0.34293 &= \text{SO}_3. \\ \text{SO}_3 \times 2.30032 &= \text{ZnSO}_4. \\ \text{SO}_3 \times 3.78416 &= \text{PbSO}_4. \\ \text{ZnSO}_4 \times 1.87638 &= \text{PbSO}_4. \\ \text{PbSO}_4 \times 0.53294 &= \text{ZnSO}_4. \end{aligned}$$

Estimation of Sulphur Dioxide (SO_2).—Weigh out 5 grams of the sample and transfer to a 400 c.c. flask, add 20 c.c. N/20 standard iodine solution, 100 c.c. water and 20 c.c. of 50 per cent. H_2SO_4 ; allow to stand for ten minutes with occasional shaking. Now add 5 c.c. freshly made starch solution and titrate with N/20 standard sodium thiosulphate. 1 c.c. I_2 = 0.0032 gram SO_2 .

Combined water and CO_2 , ferric oxide and cadmium are

determined as previously described under Zinc Oxide, the zinc oxide being taken by difference. The following is the analysis of a leaded direct process sample:

					<i>Per Cent.</i>
Moisture at 105° C.	0.085
Combined water and CO ₂	0.175
Insoluble matter	0.012
Lead oxide	2.760
Cadmium oxide	0.063
Ferric oxide	0.020
Sulphur trioxide	0.796
Sulphur dioxide	0.107
Zinc oxide (by difference)	95.982

100.000

Lithopone.—This material was originally introduced on the market in 1874, and is also known as enamel white, Charlton white, Orr's zinc white, and Griffiths' patent white, and is a compound of barytes and zinc sulphide. Lithopone is soft in texture. It unfortunately had, when first introduced, certain defects, one being its darkening when exposed to light, and the second its bad wearing properties when used for outside painting due to chalking and flaking. Modern manufacture and research have overcome many of these defects. The presence of lead, manganese, or copper causes this pigment to turn grey. Cadmium causes yellowing.

Lithopone is insoluble in water, ammonia, and alcohol. Hot dilute hydrochloric or nitric acid dissolves out the zinc sulphide and zinc oxide, leaving the barium sulphate. The zinc can be detected in the usual manner described under Zinc Oxide.

The specific gravity ranges from 3.695 to 4.325, average gravity being 4.244.

The percentage of oil required for grinding to a medium stiff paste varies in different qualities from 11 to 23 per cent. The covering power and body will vary according to the amount of zinc sulphide content; the higher the zinc sulphide the greater the covering power and body and *vice versa*. The possible adulterations are extra barytes, blanc fixe, gypsum, and chalk.

When hydrochloric or sulphuric acid is added to lithopone, sulphuretted hydrogen is given off, having a smell like rotten eggs, and a piece of test paper impregnated with lead acetate

solution will turn black. The best indication of extra barytes is the specific gravity.

It may also be necessary to differentiate between zinc oxide and lithopone. Suppose a case occurred where one hundred barrels of white paste paint were standing at a dock, and, though zinc oxide paste had been bought, some of the paste was suspected of being lithopone. The consignment should be sampled in the following manner: All the barrels should be opened, and small dabs of the paste placed and numbered on a white porcelain tile. Now spot each sample with a solution of silver nitrate containing nitric acid in moderate excess. The silver nitrate will turn the lithopone black, but the zinc oxide will be unaffected. Should any samples prove to be lithopone, these can be picked out and submitted to a more complete examination by the laboratory staff.

The following are analyses of lithopones made by the author :

<i>lithopone.</i>			<i>Barium Sulphate.</i>	<i>Zinc Sulphide.</i>	<i>Zinc Oxide.</i>	<i>Barium Carbonate</i>
1	70.12	29.02	0.73	—
2	70.93	26.60	1.66	—
3	66.40	29.36	2.70	0.98
4	70.60	26.28	1.42	0.17
5	70.65	26.52	2.26	0.32
6	69.74	26.24	3.36	0.13
7	66.70	29.64	1.55	0.36
8	75.32	21.54	0.35	0.13
9	58.16	37.42	2.14	0.22
10	63.28	33.92	2.18	0.31
11	80.80	15.58	0.28	0.22
12	71.30	25.06	1.30	0.25

A simple and useful quantitative test for lithopones by which the zinc sulphide can be rapidly estimated was devised by H. M. Rheim (*Farben Zeit.*, 1932), and is carried out as follows: The moisture is first determined by carefully weighing out 1 gram of the pigment into a previously weighed silica crucible and heating for two hours at 100° C. in a hot-water oven. The sample is then taken out, placed in a desiccator, cooled and weighed. Again place in the oven for half an hour, and reweigh. The loss in weight multiplied by 100 and divided by the weight taken will give the percentage of moisture in the sample.

Now take the dried sample and strongly ignite the crucible for forty-five to sixty minutes and, after cooling as before, weigh the crucible. The loss in weight from the previous weight obtained after the moisture determination, divided by the original weight (dried sample) and multiplied by 606.34, will give the percentage of zinc sulphide in the lithopone. This method is only applicable to genuine lithopones.

Specific gravity	3.695-4.325
Refractive index	1.84
Oil absorption	11-23
Particle size	0.25-0.35 micron.

Quantitative Estimations.

Moisture.—Determined as described under Zinc Oxide.

Procedure after F. L. Jameson, *Paint Manufacture*, August, 1939.

Barium Sulphate.—Treat 1 gram of the pigment with dilute HCl, and warm to effect solution of the soluble matter. Filter through a close-grain paper (Whatman No. 40 or 30), wash well with boiling water, dry in oven, and ignite the paper and precipitate in a silica crucible. Cool in a desiccator and weigh. The residue should consist of barium sulphate (BaSO_4). As a check, this may be fused with a mixture of sodium and potassium carbonates in a platinum crucible, and the melt when cooled extracted with boiling water. The insoluble matter is filtered off, washed with hot water, and dissolved in HCl. The barium is then precipitated from the boiling solution by the addition of a slight excess of H_2SO_4 . The filtrate from the extraction is acidified with dilute HCl, brought to the boil, and then the sulphuric acid precipitated with barium chloride. The two precipitates should be of equal weight, and together be equal to twice the amount of barytes in the original material.

Sulphur as Sulphide.—Weigh out 1 gram of the sample into a 250 c.c. beaker and add 20 c.c. distilled water. Now add 2 c.c. bromine and warm slightly until the supernatant liquid is coloured a deep red. Add dilute HCl very cautiously a few drops at a time; the H_2S is oxidised to H_2SO_4 by the bromine. Should any sulphur separate out, it can be taken up into solution by the addition of a little more bromine or a few crystals of KClO_3 . Now bring up to the boil, and allow to

stand hot until the insoluble barium sulphate has completely settled. Filter off the latter, washing the residue well with boiling water, and bring the filtrate to the boil; while still boiling, add 20 c.c. of a 10 per cent. solution of barium chloride, and continue to boil for about five minutes, and then stand the beaker on the edge of the hot plate to settle. Filter off the precipitate, wash well with hot water, and dry in oven, then ignite in a silica crucible, cool and weigh the barium sulphate:

$$\text{BaSO}_4 \times 0.13734 = \text{sulphur},$$

or by strong ignition the zinc sulphide in the pigment is converted to zinc oxide, so that if 2 grams of the sample are ignited for an hour in a muffle furnace, the loss in weight multiplied by 100 will be equivalent to the sulphur present. (*Note.*—The atomic weight of sulphur is 32, while that of oxygen is 16—exactly half.) The residue from this trial can be used for the determination of the zinc.

Zinc Determination.—Digest the residue from the ignition trial just described with about 20 c.c. of dilute (50 per cent.) HCl and filter off the insoluble residue. To the filtrate add about 3 grams of solid ammonium chloride, and make just alkaline with ammonia. Neutralise the solution with HCl and add 3 c.c. HCl in excess. Now make up the bulk to 300 c.c. with hot water, and bring to the boil, and at once titrate with a standard solution of potassium ferrocyanide, using uranium nitrate as indicator as previously described under Zinc Oxide. The actual zinc found is checked against the sulphur previously estimated, 32 parts by weight of sulphur being equivalent to 65.37 parts of zinc. Any excess of zinc will be present as zinc oxide. This can be confirmed by treating 1 gram of the sample with ammoniacal ammonium chloride solution and filtering. All the zinc oxide present will be in the filtrate, which can be acidified and titrated with standard potassium ferrocyanide.

Another method is as follows (J. Stewart Remington and Claude Smith, *J. Soc. Chem. Ind.*, 1909, xxviii, 1049): Take 0.5 gram of the sample and add 25 c.c. water at 40° C. Now add 0.5 gram bromine and cover with a watch glass and set aside for one hour, during which period the sample is occasionally agitated. Now add 10 c.c. HCl, and heat to expel excess of bromine. Now add 25 c.c. water and boil, allow to settle,

filter, and wash the barium sulphate with boiling water, dry, ignite and weigh. The filtrate is precipitated with barium chloride, and the barium sulphate formed is weighed, the amount of zinc sulphide being calculated from the weight of barium sulphate obtained.

$$\text{Barium sulphate} \times 0.32169 = \text{ZnS.}$$

Total Zinc.—Take 0.5 gram of the sample and treat with HCl (1 in 1) and boil off the H_2S ; add a little dilute H_2SO_4 . Again boil and precipitate the zinc as carbonate and weigh as oxide. The total zinc less the weight of zinc oxide, corresponding to the zinc sulphide found, gives the content of zinc oxide. As it is now some years since this method was published, the total zinc is more advantageously determined as given in the former method by standard potassium ferrocyanide. If salts of iron are present, these should be removed before the estimation of the zinc.

Titanium Oxide.

Specific gravity	3.5-4.35 (varies with grade)
Refractive index	2.76
Oil absorption ..	17-30
Particle size ..	0.28-0.39 micron

Titanium white (TiO_2) is manufactured from the mineral ilmenite, a compound of iron oxide and titanium dioxide (FeO.TiO_2). Pure titanium white contains only a small proportion of barium sulphate, but the pigments usually used in paints consist of titanium dioxide with varying proportions of barium sulphate, which may be 25 per cent. of TiO_2 and 75 per cent. BaSO_4 . There is also a calcium base pigment containing 30 per cent. TiO_2 and 70 per cent. of CaSO_4 . Within recent times various grades to fulfil specific purposes have been reintroduced, such as titanium whites which will resist after-yellowing in baking enamels, and others which will resist chalking, and are specially suitable for exterior house paints and so on. When ground on a triple roller mill the oil absorption is about 23 per cent., but if ground by stones, as is often done in America, the oil absorption may be reduced to 17 per cent. This pigment has exceptional body and covering power, and paints made with titanium have nearly twice the opacity when compared with those made with white lead. Moreover,

the paints retain their colour under all conditions. Titanium white is not affected by acids or heat, nor do sulphur fumes have any action upon it. The most reliable way is to fuse a small portion with ten times the amount of alkaline sulphates in a platinum crucible over a blast burner, and after the melt has become quite clear allow it to cool, and dissolve out with dilute sulphuric acid (1 in 1). Having obtained the titanium in solution, the following tests can be applied. Ammonia, potassium, or sodium hydroxide precipitates titanium hydroxide as a voluminous white precipitate, the precipitate being soluble in alkaline carbonates, especially ammonium carbonate.

Potassium ferrocyanide gives in slightly acid solutions a reddish-yellow precipitate, while tannin produces a brown changing to orange-red.

Hydrogen peroxide produces a yellow coloration in the presence of H_2SO_4 or HCl .

Quantitative Analysis.

Barium Sulphate.—Take 0.5 gram of the pigment and place in a 250 c.c. Pyrex glass beaker and add 20 to 25 c.c. H_2SO_4 and 8 grams of solid ammonium sulphate. Mix well with a glass rod, and heat on the hot plate until sulphuric anhydride fumes are given off, and then heat directly over the Bunsen flame for about five minutes until the solution is complete. Any insoluble left will be SiO_2 traces and BaSO_4 . Now cool, add 100 c.c. water, boil, and filter off the BaSO_4 , washing with a 5 per cent. solution of H_2SO_4 to remove the last traces of titanium, and then wash with boiling water. Reserve this filtrate for the titanium, dry the residue (BaSO_4), cool and weigh.

Calcium Sulphate.—Weigh out 0.5 gram of the pigment and place in a 250 c.c. beaker. Extract the calcium sulphate by boiling with 25 c.c. HCl (1 in 1) for about ten to fifteen minutes. Now dilute with water 150 c.c., boil and filter. Wash the residue on the filter with a hot 10 per cent. solution of HCl until the washings show no trace of calcium, and then determine the calcium by precipitating with ammonium oxalate, having first added ammonia to make the liquid distinctly ammoniacal.

Boil the liquid and allow the beaker to rest on the hot plate for half an hour, then wash three or four times by decantation, finally transferring the precipitate to the filter and wash well

with boiling water. Transfer the precipitate and paper to a beaker and add 50 c.c. 10 per cent. solution of H_2SO_4 , boil and titrate with N/10 potassium permanganate to a faint pink.

1 c.c. of the standard permanganate = 0.0028 CaO, and this multiplied by 2.4286 gives the $CaSO_4$.

Titanium Dioxide.—Take the filtrate from the barium sulphate estimation and evaporate down to 100 c.c. This requires reducing to the titanous state, and is carried out in the apparatus illustrated as recommended by Mr. Noel Heaton.

The section A is charged with zinc amalgam to a height of about 3 inches, and is well washed with hot water. The bottom part of the reducer near the tap E is filled up with water to the point or level B. This precaution is necessary in order to prevent any of the titanium escaping contact with the zinc. The acid solution of titanium—that is, the original filtrate from $BaSO_4$ estimation—is placed in the cup C. A small separating funnel is equally convenient, and the solution is run on to the zinc amalgam in section A. Hydrogen is at once evolved, and after about fifteen minutes the titanium is reduced to the titanous condition. A freshly prepared solution of 5 c.c. potassium sulphocyanide is placed in the flask D, which is then connected with the reducer and a stream of CO_2 is passed into the flask by the tube (H), and when all the air has been removed the titanous solution, now a purplish-blue colour, is run into the flask D by means of the tap E, and the reducer washed through four times, using 25 c.c. of water each time. The flask is then disconnected, and the contents at once titrated with a solution of standard ferrous ammonium sulphate, the CO_2 being maintained during the titration; 1 c.c. of this standard solution = 0.005 TiO_2 . The standard ferrous ammonium sulphate is made by dissolving 30 grams of the salt in 300 c.c. water,

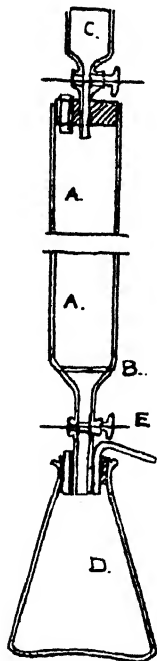


FIG. 3.

acidifying with 10 c.c. H_2SO_4 , and then adding N/10 standard potassium permanganate drop by drop until a faint pink colour remains on shaking. This is done to oxidise any ferrous iron to ferric, and the solution is then made up to 1,000 c.c. The zinc amalgam is made by coating pure granulated zinc made from electrolytic spelter with metallic mercury; by immersing the zinc in a 5 per cent. solution of mercuric chloride, warming the solution, and leaving the zinc in contact for about five to ten minutes. The zinc is then taken out and well washed with water.

The following gravimetric method (Elmer B. Schuler) is very suitable for paint works who are not doing titanium estimations every day, and saves the trouble of setting up and preparing a reducer as required when carrying out the volumetric method previously described: Take 0.5 gram of the sample and place in a 400 c.c. Pyrex beaker, add 5 grams Na_2SO_4 or 7 grams $(\text{NH}_4)_2\text{SO}_4$ and then 20 c.c. H_2SO_4 . Heat over a flame until the solution clears. Heat gently at first, as the mixture will foam, but when this has ceased, heat strongly. Cool and add 200 c.c. water, and then boil for twenty minutes. Filter hot and wash with 5 per cent. solution H_2SO_4 .

The residue on the filter will be $\text{SiO}_2 + \text{BaSO}_4$. The filtrate will contain the titanium, zinc, iron, and aluminium. To the filtrate add while hot NH_4OH in excess, then filter and wash well with boiling water. Redissolve the precipitate in HCl and again add NH_4OH , filter, and again wash with boiling water. Join the two filtrates together. If no iron and aluminium are present, the precipitate may be dried, ignited and weighed as TiO_2 . On the other hand, if iron and aluminium are present, the precipitate must not be ignited, but dissolved in HCl . To the solution add NH_4OH slowly until the solution is very nearly neutral. This will be shown by a slight cloudiness appearing, but on well stirring it will become clear again. Now add 1 c.c. of a 10 per cent. solution of $(\text{NH}_4)_2\text{SO}_4$, 5 c.c. glacial acetic acid; then add 15 grams ammonium acetate and make up to 350 c.c., and boil for three minutes. The titanium will separate out as a white flocculent precipitate. Filter and wash with water containing 5 per cent. acetic acid, and finally wash with distilled water. Then dry, ignite and weigh as TiO_2 . The filtrate can be used for the estimation of the zinc and is best determined as pyrophosphate.

Titanated Lithopone.—These pigments are found in the United States and usually consist of about 25 per cent. zinc sulphide, 59 per cent. barium sulphate and 15 per cent. titanium oxide. The specific gravity varies from 4.19 to 4.25, and the oil absorption from 11.3 to 19.5 per cent.

Antimony Oxide.

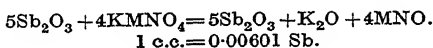
Specific gravity .	5.43-5.75
Refractive index	2.09-2.29
Oil absorption .	11.2-11.6
Particle size .	0.29-0.34 micron

This pigment, which has come into prominence during the last eighteen to twenty years, is antimony oxide or antimonious oxide (Sb_2O_3), and is chiefly manufactured from stibnite (Sb_2S_3), known to the trade as grey antimony. Antimony oxide has a pure white colour and requires on the average 11 per cent. of oil to grind it into a stiff paste. Under the microscope the powder is seen to have a fine crystalline structure, and is of soft texture, being entirely soluble in hydrochloric acid. In the presence of sulphuretted hydrogen (H_2S) a paint film containing this pigment turns yellow. The trade name for antimony white is "Timonox." "Timonox" Red Star is the pure pigment 99.100 per cent. Sb_2O_3 , but lower grades are mixtures of antimony oxide and zinc oxide, or of antimony oxide, zinc oxide and barytes.

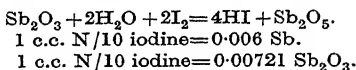
Zinc oxide assists antimony white to a considerable extent by preventing "chalking," improving the hardness and weather properties of the film. The amount of zinc oxide to be added may vary from 5 to 50 per cent., according to circumstances. In order to detect antimony, dissolve the powder in HCl , being careful not to have too great an excess, and pass H_2S through the solution. A flocculent orange-red precipitate of antimony trisulphide (Sb_2S_3) will be thrown down, and this is soluble in ammonium sulphide and caustic alkali. On dissolving the pigment in hydrochloric acid and then pouring the solution into a beaker of distilled water a white precipitate of antimony oxychloride ($\text{Sb}_4\text{O}_5\text{Cl}_2$) will be produced. Both these tests are characteristic of antimony.

Quantitative Estimations.

Weigh 1 gram of the reduced antimony pigment or 0.5 gram of the pure pigment into a Pyrex beaker 250 c.c., add 20 c.c. HCl and 5 c.c. water, put on a cover glass and heat on a sand bath or a steam bath for fifteen to twenty minutes, cool, carefully washing the cover glass, and then add 3 grams of tartaric acid and 100 c.c. hot water, and digest on the sand bath for about five minutes; then filter, collecting the filtrate in a 500 c.c. beaker, and washing the residue on the filter with boiling water. The residue will most likely be barium sulphate (BaSO_4). Dilute the filtrate with 250 c.c. hot water and pass in H_2S for about fifteen minutes. Filter the precipitate, washing with H_2S water, then return the precipitate to the beaker, add 15 c.c. H_2SO_4 and 10 grams K_2SO_4 , and heat until the solution is colourless; cool, dilute to 250 c.c., add 20 c.c. HCl (sp. gr. 1.19), and boil for three minutes; cool to 10°C ., and titrate to a faint pink with N/10 potassium permanganate.



Another method is to weigh 0.5 gram of the sample into a 500 c.c. beaker, add a solution of tartaric acid, which will dissolve the antimony oxide on boiling, cool, add solid sodium carbonate little by little and then an excess of sodium bicarbonate to make alkaline, and titrate with standard N/10 iodine, using freshly prepared starch solution as the indicator.



Another method is to dissolve the pigment in hydrochloric acid, and having removed the insoluble as previously described, add HCl until the solution contains one-third of its volume, and then add standard potassium bichromate which has been previously standardised against a solution of arsenious oxide (As_2O_3) made by dissolving 5 grams of the arsenious oxide in caustic soda, adding 100 c.c. HCl, and making up to 1 litre (1,000 c.c.). In carrying out this method an excess of the bichromate is added, and the excess titrated by standard ferrous sulphate which has been previously standardised against bi-

chromate solution, using potassium ferricyanide as indicator prepared as spots on a white porcelain tile.

1 c.c. $\text{As}_4\text{O}_6 = 0.005$ gram $\text{As}_4\text{O}_6 = 0.00725$ gram Sb_2O_3 .

Barytes.—Barytes, heavy spar or barium sulphate (BaSO_4), is sold under different grades, each varying as regards fineness of grinding and colour, known as best superfine white, seconds, and common barytes. The specific gravity ranges from 4.401 to 4.482. The oil absorption is low, being 7.5 to 9 per cent. of oil to grind into paste form. Barytes is the best known and most widely used extender in the paint trade. It has practically no covering power or body.

Barytes is insoluble in water, and is not acted upon by acids or alkalis, except to a small extent by sulphuric acid. If warmed with strong sulphuric acid, about 3 per cent. will become dissolved. If the liquid is then very carefully poured into water, the barium sulphate will become precipitated again. A simple test for colour is to place a couple of grams on a glass slab alongside a standard sample, and to add a few drops of American turpentine to each. Now mix up well, and note the resulting colour, which should be a cream white. The texture is best examined by grinding the sample moistened with turpentine on a slab with a steel palette knife. After a little practice, the texture can soon be ascertained. Should free acid be present, due to imperfect washing after bleaching in the course of manufacture, place a small quantity of the sample in a beaker, add distilled water, and then test with blue litmus solution. Should the paper or liquid turn red, the presence of acid will be indicated. Should carbonate of lime be suspected, boil a portion of the sample with a little hydrochloric acid; any effervescence will indicate carbonates. Filter off the liquid and divide into two parts. To one portion add barium chloride; a white precipitate will indicate calcium sulphate. To the other portion of the filtrate add three drops of nitric acid, and a little potassium ferrocyanide solution; a blue coloration will indicate iron. The Bunsen flame is coloured green with a yellow shade by barytes, when a sample is submitted to the platinum wire and flame test. The sample should be examined microscopically to determine uniformity of grinding and whether the particles are crystalline or amor-

phous. When examined quantitatively, barytes should not test less than 95 per cent. BaSO_4 .

The complete analysis of barytes is shown as follows:

	Per Cent.
Moisture	0.12
Barium sulphate (BaSO_4) ..	98.44
Calcium sulphate (CaSO_4) ..	0.74
Iron oxide (Fe_2O_3)	0.27
Alumina (Al_2O_3)	0.12
Magnesia (MgO)	0.08
Silica (SiO_2)	0.23

100.00

It is usually unnecessary to make such an analysis. In most cases, except for the qualitative tests previously given, the only tests which may be considered necessary are loss on ignition and also for soluble and insoluble matter.

Loss on Ignition.—Ignite 1 gram of the sample in a silica or platinum dish or crucible in a muffle for thirty minutes. The loss may be due to moisture combined water and CO_2 . Should the loss be considerable, then the CO_2 should be estimated as given under White Lead.

Soluble and Insoluble Matters.—Weigh out 1 gram into a 250 c.c. Pyrex beaker and add HCl (1 in 3), boil well, then filter. Wash with boiling water, dry in oven, ignite and weigh the residue. This residue, if desired, may be further treated with H_2SO_4 and HF in the usual manner for silica.

Blanc Fixe.—This material is precipitated barium sulphate, and is also known as permanent white and enamel white. It is supplied to the trade as a fine white powder or as a paste containing 20 per cent. of water. Blanc fixe is an amorphous powder, whereas natural barytes is crystalline. Blanc fixe can be distinguished from barytes by rubbing up the pigment with linseed oil on a piece of glass. The barytes will feel gritty under the knife, while the blanc fixe will feel smooth. The tests previously described for barytes also apply to blanc fixe. Specific gravity, 4.329 to 4.336.

Strontium Sulphate.—This material occurs naturally as the mineral celestine. During the late war it was used frequently as a substitute for barytes, but in this respect it is not very

satisfactory as it absorbs more oil. The specific gravity ranges from 3.86 to 3.90. By the platinum wire test it imparts a bright red flame with a crimson shade.

Whiting.—This product is also known as calcium carbonate, Paris white, Spanish white, English white, and chalk. It is a dull white powder of a soft amorphous character, having a specific gravity of 2.5 to 2.8. It is insoluble in water when pure, but dissolves in water containing carbon dioxide owing to the formation of soluble calcium bicarbonate. It is soluble in dilute acids with effervescence, due to the evolution of carbon dioxide, which can be proved by pouring the gas, which is heavy, into a test-tube containing lime-water, when, on shaking up, it will become milky. When heated to a red heat the carbon dioxide is driven off, quicklime (CaO) remaining.

Whiting is used mostly as a body colour for distempers and for ceiling water paints.

It is not used as an oil colour, because when mixed with linseed oil it turns a dirty grey. When mixed with 18 per cent. of linseed oil it forms putty.

Whiting is distinguished by the following tests:

(I.) It is soluble in dilute hydrochloric acid with effervescence.

(II.) On the addition of ammonium oxalate a white precipitate of calcium oxalate, soluble in acids, is formed.

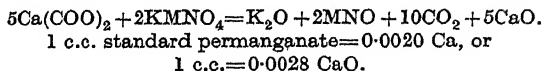
(III.) On heating, after moistening with hydrochloric acid, and holding a small portion on a platinum wire in the oxidising flame, a red colour having a yellowish to orange shade is imparted to the flame.

Today this extender may be found as natural whiting; precipitated whiting; very finely precipitated or colloidal whiting, which is a very easily dispersed variety (Multifex); and surface-treated whiting—that is, a fine whiting with a monomolecular coat of an organic acid (Surfex).

Should it be desired to determine the calcium present proceed as follows:

Weigh out 1 gram and place in a 300 c.c. beaker, and add dilute HCl (1 in 1) and a few drops of HNO_3 . Evaporate to dryness on the hot plate, then moisten with a few drops of HCl , add 100 c.c. hot water, boil and filter off any insoluble matter (which is nearly always silica), filter, dry and weigh.

Take the filtrate and precipitate the iron and alumina in the usual manner with NH_4Cl and NH_4OH . Reserve the filtrate and add 30 c.c. of a saturated solution of ammonium oxalate, and boil the solution well; allow to stand thirty minutes, then filter off the calcium oxalate and wash well with hot water. Transfer the paper and precipitate to a beaker, adding a 10 per cent. solution (about 50 c.c.) of H_2SO_4 , and titrate with N/10 potassium permanganate, the reaction being as follows:



Terra Alba.—This material is also known as gypsum, light spar, and calcium sulphate, and has the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, being hydrated calcium sulphate. The specific gravity is 2.35. One part of pure hydrous calcium sulphate is soluble in 500 parts of water.

Gypsum is soluble in ammonium chloride solution. One hundred c.c. of a 25 per cent. ammonium chloride solution will dissolve 1 gram of the calcium salt. Calcium sulphate is easily soluble in a saturated solution of ammonium sulphate, which distinguishes it from strontium and barium sulphates, which are insoluble. Hot, strong hydrochloric acid, 1.20 specific gravity, will dissolve calcium sulphate readily and without effervescence. Terra alba is used in the manufacture of lake colours, Venetian red and lime greens, also in the manufacture of lime blues from ultramarine, pulp colours and cold water paints.

Asbestine.—This is the residue or short fibre from asbestos which was formerly considered as waste. It is reduced to a fibrous pulp and sold as asbestine, and is now much used in paints to help pigment suspension. It is a magnesium silicate. The specific gravity runs from 2.30 to 2.90.

China Clay.—China clay is the only white pigment composed entirely of clay, and comes from Cornwall. It consists of silica, about 48 per cent., and alumina, 38 per cent., with small amounts of ferric oxide, lime, magnesia, and alkalis. The specific gravity is about 2.596, and the oil absorption 28.9 to 30 per cent. The following are analyses of English china clays made by the author:

<i>Sample.</i>	<i>Silica</i> (SiO_2).	<i>Alumina</i> (Al_2O_3).	<i>Ferric</i> <i>Oxide</i> (Fe_2O_3).	<i>Lime</i> (CaO).	<i>Magnesia</i> (MgO).	<i>Total</i> <i>Water.</i>	<i>Alkalies</i> (K_2O).	<i>Total.</i>
1 ..	46.21	39.82	0.38	0.45	0.10	12.81	0.23	100.00
2 ..	46.32	39.76	0.40	0.41	0.11	12.69	0.31	100.00
3 ..	47.60	38.26	0.55	0.42	0.20	12.40	0.57	100.00
4 ..	47.74	37.66	0.58	0.61	0.22	12.60	0.59	100.00
5 ..	45.74	36.84	1.86	0.60	0.11	11.06	3.79	100.00
6 ..	46.46	37.40	2.00	0.86	0.21	11.81	1.26	100.00
7 ..	48.16	38.45	2.06	0.50	0.14	10.59	0.10	100.00
8 ..	46.20	36.23	1.57	0.76	0.11	11.00	4.13	100.00
9 ..	46.60	37.48	1.26	0.64	0.22	12.74	1.06	100.00
10 ..	46.28	38.38	1.03	0.72	0.15	12.78	0.66	100.00
11 ..	46.38	39.00	0.79	0.58	0.11	12.70	0.44	100.00
12 ..	47.26	37.84	1.08	0.54	0.29	12.07	0.82	100.00

On comparing the figures of the clays marked Nos. 6, 7, and 8 with those yielded by the other samples, it is evident that there is a great difference in their iron content. A corresponding difference appears in the character of the clays, notably when compared with those marked Nos. 1 to 4 and those marked Nos. 9 to 12, which are finer and possess a much better colour. The latter variation may be partly owing to a difference in the nature and extent of the surrounding beds, or to some local circumstance affecting the cleaning of the material and the nature of the clay produced. The presence of a comparatively high percentage of alkalies in the clays Nos. 5 and 8 points to the fact that the clay is associated with an unusually large quantity of unaltered felspar and some micas, while the potash content found on analysis indicates the presence of a variety of mica known as Muscovite or of the characteristic minerals of granites or other crystalline rocks.

Kieselguhr or Diatomaceous Earth.—This is a soft pulverulent material, being found in colour from a grey buff to a white product. Its origin is due to aquatic forms of plant life known as diatoms which have been laid down in past ages and possessed the property of secreting silica. On the death of the plants the silicious skeletons are left at the bottom of lakes and tarns, producing in time beds of considerable thickness. The specific gravity of kieselguhr is 2.8. It has been stated by

Dr. Henry A. Gardner that the addition of this inert assists in allowing paints and damp wall preparations to breathe, and produces a film from which internal moisture escapes.

Other extenders which from time to time are used are fine amorphous silica, of which milowite is a good example, containing over 98 per cent. of SiO_2 , and being quite free from iron. In addition there are such products as mica, a magnesium silicate ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$) which, on account of its leafing properties, is becoming popular in various special paint formulations. In addition we have steatite or soap stone, slate powder, and several other products used in a minor degree.

In the case of all these inerts a chemical analysis is unnecessary. What is much more important is the determination of the specific gravity, relative density, settling test in white spirit, a careful microscopical examination to determine the particle size and particle shape, also noting the texture, whether it is soft like whiting or hard like silica, and the oil absorption, for it must be remembered that paints are considerably affected by the kind and amount of extender used. They all have a direct bearing on such questions as settling and caking, consistency, gloss, hiding power, washability, surface adhesion, resistance to corrosion, and durability of the resulting paint, and require careful thought and study as regards the formulation of a paint for a particular job.

Alumina.—This is also known as alumina white; it has the formula $\text{Al}_2(\text{OH})_6$ and is largely used as a base for lake colours. It dissolves easily in dilute acids, also in caustic alkali. If the alumina is dissolved in caustic soda and then the liquid is made acid with hydrochloric acid, and ammonia added, the alumina will be precipitated as a white gelatinous mass insoluble in ammonia.

SECTION II
SIMPLE TESTS FOR COLOURED PIGMENTS

Ochres, Oxides and Siennas.

Yellow Pigments.

Ochres.—The chief yellow pigments are yellow ochre, raw sienna, and the various shades of lead chromes, zinc chrome, and barium chrome. The yellow ochres are widely distributed. They are essentially silicates of alumina coloured by iron hydroxide. The best known are the French, Indian, Spanish, Italian, and English. Prepared ochres are pigments of soft texture and very permanent, with fairly good covering power. The average specific gravity is 2.80.

Poor-coloured ochres are frequently fortified by the addition of chrome yellow. When a yellow ochre is heated it turns red, due to the fact that the yellow ferrous hydrate is changed to the red ferric oxide. To test an ochre suspected of being toned up by chrome, dissolve about 1 gram in hydrochloric acid and pass sulphuretted hydrogen; a black precipitate of lead sulphide (PbS) will be produced.

Ochres are generally tested for strength and oil absorption. When testing for strength, take 1 gram of the ochre and mix it with 10 grams of zinc oxide. Now add a measured quantity of refined linseed oil drop by drop from a burette, and then compare on a glass in a north light with a standard sample similarly treated. When testing for oil absorption, a quick and rough way is to weigh out 1 gram of the ochre on to a porcelain testing slab; then add refined linseed oil drop by drop from a burette, working up the ochre with a palette knife. The addition of oil is stopped when the ochre is converted into a stiff paste. Proceed in a similar manner with a standard sample, and count the drops of oil in each case that are required to get an equal consistency.

French ochres are sold under the brands: J.F.L.S., J.F.L.E.S., J.F.L., and J.C., etc., in casks of 340 and 360 kilos gross

weight. J. stands for jaune, or yellow; L. for lave, or levigated; E. for extra; F. for foncé, or dark.

The percentages of oil in stiff paste ochres are as follows:

	<i>Per Cent.</i>
American ochre, yellow	28.30
French ochre	30.33
Oxford ochre	25.30

The following analyses made by the author give the approximate composition of ochres found on the market:

<i>Sample.</i>	<i>Ferric Oxide (Per Cent.).</i>	<i>Insoluble Matter (Per Cent.).</i>	<i>Moisture (Per Cent.).</i>
	45.13	39.28	1.88
	47.14	25.84	3.72
	48.28	16.80	2.34
	14.28	62.64	1.34
	69.71	12.28	3.72
	48.57	20.24	1.00
	19.43	64.30	1.20
	16.91	67.65	0.61
	16.85	59.06	1.34
10	61.13	16.15	1.84
11	24.00	56.06	1.34
12	50.86	13.20	1.21

Raw Sienna.—The best siennas come from Italy, but a certain amount is also obtained from America and Germany.

Raw sienna has a deeper tone of yellow than an ochre, and is very transparent, and on this account is largely used for staining and for graining wood. The following is an analysis of an Italian sienna:

	<i>Per Cent.</i>
Combined water	9.67
Ferric oxide	53.83
Alumina	5.86
Silica	28.25
Calcium carbonate	1.12
Magnesia	1.27

100.00

Sienna is tested for strength and oil absorption in a similar manner to ochre.

The percentage of oil required by an average Italian raw

sienna is 55, representing 135 lbs. of oil to convert 112 lbs. of pigment into a stiff paste. Burnt sienna is obtained by calcining raw sienna at a low temperature till the desired shade is produced. Burnt Italian sienna requires 50 per cent. of oil to produce a stiff paste. Siennas should be finely levigated, should contain not less than 50 per cent. of iron (calculated as ferric oxide), and should have a good undertone and transparency.

Quantitative Estimations.

The analysis of ochres, raw and burnt sienna, natural iron oxides, and synthetic oxides and ochres can be carried out as follows:

Moisture.—Take 2 grams of the sample and place in a previously weighed wide-mouthed weighing bottle and heat in a water oven for one hour at 105° , then cool and weigh. Replace in the oven for thirty minutes, then cool and weigh again. If of constant weight, calculate the moisture in the usual manner.

Loss on Ignition.—Take 1 gram of the previously dried sample and ignite in a covered silica crucible to constant weight. The loss will include combined water, CO_2 , and organic matter as a general rule, but should the original sample contain a fair proportion of calcium sulphate, this can be ascertained by making a qualitative analysis. There may also be loss due to SO_3 .

Insoluble Matter and Iron Oxide.—Take 2 grams of the previously ignited sample which has been treated at a low temperature to destroy the organic matters, if any, and place in a 250 c.c. Pyrex beaker, add 25 c.c. HCl and a few drops of HNO_3 and evaporate to dryness over the hot plate, then allow to cool. Take up with dilute HCl (1 in 1), boil, filter, and wash four times with 5 per cent. HCl solution and then ten times with hot distilled water. Dry the residue, ignite and weigh the insoluble matter—chiefly SiO_2 —in the usual manner.

Take the filtrate and transfer to a 500 c.c. measuring flask and make up to the 500 c.c. mark. Now take 100 c.c. of this filtrate and place in a 500 c.c. beaker, add 2 c.c. stannous chloride and 15 c.c. HCl, cover with a watch glass and heat on the hot plate for about fifteen minutes, when the solution should be complete. Now add 10 c.c. of "preventive solution" and 250 c.c. cold water which has been recently boiled and

allowed to go cold, and then at once titrate with N/10 potassium permanganate. The best and safest way is to add the permanganate slowly and with constant stirring at such a rate that the drops can be counted, and the standard solution must be added until the first pink coloration will last for about three or four seconds. 1 c.c. of N/10 $\text{KMnO}_4 = 0.007984$ gram ferric oxide (Fe_2O_3).

The "preventive solution" is as follows: 3.2 grams manganese sulphate are dissolved in 35 c.c. of water and 6 c.c. of phosphoric acid (sp.gr.1.7) and 5 c.c. H_2SO_4 added. Unless this "preventive solution" is present there is in the titration an evolution of chlorine produced by the oxidation of the HCl by the permanganate in the presence of iron salts, and in that case higher results are likely to be obtained. The action may be explained as regards "the preventive solution" that the permanganate forms with the manganese sulphate manganese dioxide, which reacts more rapidly with the ferrous salt than it does with the HCl. The phosphoric acid is added to change the yellow ferric chloride, which might obscure the end point into colourless ferric phosphate.

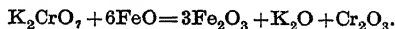
The iron can also conveniently be determined by N/10 standard potassium bichromate, using potassium ferricyanide as the indicator.

Take the filtrate from the insoluble as previously described, pipetting out 100 c.c., and place in a porcelain dish and bring up to the boil. Now add stannous chloride drop by drop till the colour changes due to the ferric iron being converted to ferrous, being careful not to add an excess, otherwise a milky precipitate will result. Now add 100 c.c. distilled water, and as soon as the solution is quite cold (adding some small pieces of ice is a good thing) 5 c.c. of mercuric chloride solution is added to insure the removal of any excess of stannous chloride, when a slight milky precipitate will form. Now titrate with the bichromate solution, having the ferricyanide solution spotted on a white testing tile. When the solution, withdrawn by a glass rod, is applied to a test spot and shows a faint blue the titration is finished.

1 c.c. of potassium bichromate $= 0.00798 \text{ Fe}_2\text{O}_3$.

The N/10 potassium bichromate is made by taking 4.9033 grams of the salt and making up to 1,000 c.c., standardising

this against pure iron wire or ferrous sulphate. The reaction by this method is as follows:



Alumina.—To 100 c.c. of the filtrate from the insoluble determination add ammonium chloride and ammonia and boil well. Then allow to settle, filter off, and wash well with boiling water ten times. Dry the precipitate, ignite in a weighed silica crucible, cool, and weigh the combined ferric oxide and alumina, deducting the iron oxide previously found, and obtain the Al_2O_3 by difference.

Calcium.—To the filtrate from the iron oxide and alumina add ammonia and ammonium oxalate and boil the solution well, then filter. Wash the precipitate and dry in oven, then place in a weighed silica crucible, ignite, cool and weigh as calcium oxide (CaO).

Magnesia.—To the filtrate from the calcium estimation add a solution of sodium hydrogen phosphate. Stir the solution vigorously with a glass rod and allow to stand for about six hours, when all the magnesia should have been precipitated; then filter, wash, and dry as before, ignite, cool, and weigh the $\text{Mg}_2\text{P}_2\text{O}_7$. Amount of $\text{Mg}_2\text{P}_2\text{O}_7 \times 0.3620 = \text{MgO}$.

Sulphates.—Take 1 gram of the sample dissolving in HCl or take 100 c.c. of the filtrate as originally stated, remove the iron and alumina as if estimating the alumina. To the filtrate add 10 c.c. hot barium chloride solution, boil well, and allow to rest on the hot plate for about thirty minutes; then filter, washing ten times with boiling water; then dry, ignite, cool, and weigh, calculating to calcium sulphate. $\text{BaSO}_4 \times 0.5837 = \text{CaSO}_4$.

Chrome Yellow.—Chromate of lead (PbCrO_4) comes on the market in various shades as primrose chrome, lemon chrome, middle chrome, orange chrome, and chrome red, which latter variety also goes under the names of Persian red, Chinese red, and Derby red.

The chromes are pigments possessing remarkably good body and brightness in tone. They are soft in texture, with the exception of Persian red, which is generally rather crystalline in nature. The chromes are readily affected by alkalis, turning to an orange colour. They are darkened by sulphuretted hydrogen, or when spotted with ammonium sulphide on a test slab.

When treated with dilute nitric acid they should be entirely soluble, but should a reduced chrome be so treated and barytes or gypsum suspected, a residue would be left on the filter, which can be verified by the flame test.

The strength of a chrome is best ascertained by adding a definitely weighed quantity of Chinese blue and comparing the green shade obtained against a standard sample treated in a similar manner. When purchasing chrome yellows, the pigment should conform to the following specification :

- (I.) It should contain 90 per cent. of lead compounds.
- (II.) It must be soft in texture.
- (III.) It must be equal in shade and brightness to the approved sample.
- (IV.) When reduced with ten times its weight of zinc oxide in refined linseed oil, the shade should be equal to a standard sample treated in a similar manner.
- (V.) It must not contain more than 2 per cent. of matter soluble in water.

The percentages of oil in stiff paints are :

							<i>Per Cent.</i>
Lemon chrome	20
Middle chrome	26
Orange chrome	22

Zinc Yellow.—Zinc chrome (ZnCrO_4) is a bright yellow pigment of pale shade, and is soluble in all mineral acids. When heated it changes to a dark purple colour, due to the decomposition of the zinc oxide and chromium oxide. It is an excellent yellow for tinting distempers, as it is not affected by lime or sulphuretted hydrogen. The difference between a pale lead chrome and a zinc chrome can easily be ascertained by the action of dilute acetic acid, in which the zinc chrome is soluble, whereas the lead chrome is not. Zinc chrome has rather a poor body when compared with lead chrome, but with Chinese blue these chromes form an excellent range of non-poisonous zinc greens. A really well made zinc chrome should not be hard when rubbed up with refined linseed oil, nor should it become grainy. Pure zinc chrome will require 22-24 parts of linseed oil by weight to 76-78 parts by weight of pigment. A very simple test is to boil the sample of chrome with distilled

water; the zinc chrome, being somewhat soluble, will give a yellow filtrate, while lead chrome, being insoluble, will give a colourless filtrate.

Lead and Zinc Chromes : Quantitative Estimations.

Moisture.—Heat 2 grams of the sample in a hot-water or electric oven at 105° C. for two hours, and report in the usual manner.

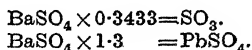
Chromium Oxide (CrO_3).—Dissolve 0.5 gram of the dried sample in 20 c.c. of a saturated solution of NaCl (Saxa salt) containing 10 per cent. HCl. Now add 3 grams of potassium iodide and 5 c.c. starch solution, and titrate with N/10 sodium thiosulphate. 1 c.c. = 0.0033 gram CrO_3 .

Lead Oxide (PbO).—To determine the lead in lead chromes dissolve 0.5 gram contained in a 400 c.c. beaker by means of HCl, adding 10 c.c. dilute H_2SO_4 (50 per cent. solution), and evaporate slowly on the hot plate until fumes of sulphur trioxide are given off. Take off the beaker and allow it to cool, and then moisten with 10 c.c. cold water. Now add 100 c.c. boiling water and boil for ten minutes, and then allow to stand cold for about three and a half hours. Filter off the precipitate, wash with 5 per cent. H_2SO_4 solution, then transfer to beaker with 5 grams of ammonium acetate dissolved in 100 c.c. hot water, and boil until the lead has dissolved, washing the filter paper also with ammonium acetate solution and adding the washings to make sure that no lead is lost. To the boiling solution add 100 c.c. of a saturated solution of potassium dichromate and continue boiling for about thirty minutes. The lead chromate will easily settle, and will have changed from yellow to a dark orange or brick red. Filter off the lead chrome through a Gooch crucible charged with a plug of filter-paper pulp, washing the precipitate with the special salt solution (as used in the case of white lead) into a conical flask, then add a little more salt solution to the flask to complete the solution of the precipitate. Add 3 grams of KI and a few c.c. of freshly prepared starch solution and titrate with N/10 standard sodium thiosulphate. 1 c.c. = 0.007433 gram PbO .

In the case of zinc chromes, the zinc can be estimated as follows: Dissolve 1 gram of the sample in HCl, dilute with hot water, and pass SO_2 gas until the solution goes green or add some crystals of sodium sulphite. Boil to expel excess of gas,

cool, and neutralise with NH_4OH . Now add 3 grams of NH_4Cl and then 4 c.c. HCl and make up the bulk to 300 c.c.; boil and titrate with potassium ferrocyanide, using uranium nitrate as indicator on a spot plate as outlined under zinc oxide. Another method is to dissolve 1 gram of the sample in the hydrochloric plus salt solution as used in the estimation of lead by the bichromate method previously described, dilute with 150 c.c. hot water, and add 15 c.c. of a 10 per cent. solution of lead acetate. Now add ammonia until the solution is alkaline, boil and allow to settle. Filter off the lead chromate and estimate the zinc in the filtrate in the usual manner.

Sulphur Trioxide (SO_3).—In the case of lead chromate the presence of sulphur trioxide would indicate the addition of lead sulphate, while in the case of zinc chromes that sulphuric acid or zinc sulphate had been used. This applies to soluble sulphates only. Dissolve 1 gram of the sample in 10 to 15 c.c. HCl , filter if necessary, dilute with 150 c.c. hot water and boil. Now add 10 c.c. of a 10 per cent. solution of hot barium chloride and boil for about ten minutes, and allow to stand on a corner of the hot plate to keep warm for about three hours, then filter. Wash ten times with hot water, dry, ignite and weigh.



Insoluble Matter.—Dissolve 1 gram of the sample in 25 c.c. HCl and boil for about eight minutes, then filter, washing well with boiling water; then dry, ignite and weigh in the usual manner. The insoluble will consist of barytes, and in addition there may be traces of silica which may be ignored.

Added Colouring Matters.—Treat a sample of the pigment successively with hot water, 95 per cent. alcohol and chloroform. The solution should remain colourless after filtering, but the above treatment will indicate if any aniline yellow has been added to fortify the pigment. This sometimes occurs in the case of zinc chromes.

Barium Chrome.—Barium chrome has the formula BaCrO_4 . It is a pigment of a pale yellow colour, and is deficient in body. It is not affected by sulphuretted hydrogen, and is permanent to light. It is decomposed by strong acids and alkalis. The barium can be verified by the flame test; colour green, shade yellowish. It is chiefly used in paper staining.

Other yellow pigments chiefly used by artists are Naples yellow, cadmium yellow, King's yellow, and aureolin. *Naples yellow* is a compound of antimony and lead oxides, but was originally a volcanic product. It is little used at the present day. A substitute made by mixing cadmium yellow with white has been found to be more satisfactory. Naples yellow is made in two shades, pale and deep. This pigment requires 14-18 parts by weight of oil to 85-86 parts by average weight of pigments to produce a stiff paste.

Cadmium yellow is chiefly used by artists and appears on the market in three shades—pale, medium, and orange. The darker shades are permanent to light, but the pale varieties frequently contain either zinc sulphide or zinc oxide. Pure cadmium yellow dissolves in a strong warm solution of hydrochloric acid to a clear liquid giving off sulphuretted hydrogen. When chrome yellow is mixed with cadmium yellow it will give a black precipitate of lead sulphide when treated with a solution of sodium sulphide. The specific gravity is about 4.359 and the oil absorption 16.5 to 18 per cent.

King's yellow is a sulphide of arsenic, also known as orpiment, and is only used by artists.

Aureolin is a double nitrate of cobalt and potassium, $K_2Co(NO_3)_4$. It is a transparent yellow of moderate permanence requiring 6 parts by weight of oil to 4 parts of pigment. The cobalt can be tested for thus: Make a saturated solution of α -nitroso- β -naphthol ($C_{10}H_6(NO)OH$) in a 50 per cent. solution of acetic acid. Take some of the pigment assumed to be aureolin, add dilute hydrochloric acid and some dilute acetic acid, then add the freshly prepared reagent; should cobalt be present, a voluminous purple-red precipitate of cobalti-nitroso- β -naphthol will result.

Blue Pigments.

The chief blue pigments used by the paint trade are ultramarine, lime blue, Prussian blue, and cobalt blue. Other blue pigments were at one time used, such as Bremen blue and blue verditer, but these have now become obsolete as regards the decorative trades.

Ultramarine.—The composition of this well-known pigment has never been definitely settled. Hoffmann assigns to it the formula $2(Al_2Na_2SiO_{10}).Na_2S_4$. It is also known as French

ultramarine blue, new blue, and permanent blue. Ultramarine is a colour of good permanency, being used as an oil paint whitener, and for tinting. It is not affected by alkalis nor heat, but the blue colour is at once discharged by acids, sulphuretted hydrogen being evolved and sulphur thrown down. There are various grades of ultramarine, which are best tested for tone, shade, fineness, and softness by the usual methods. Rubbing out 1 part of blue with 25 parts of zinc oxide is a very good guide. When grinding ultra blue in oil, a blue having the strongest staining power should be selected, and the average mixture will require two-thirds by weight of pigment to one-third by weight of oil. When grinding ultramarine, refined oil should be used in preference to raw or boiled oil, as it gives the ultra blue a cleaner tone and appearance. The chemical analysis of ultramarine is seldom asked for.

Lime Blues.—This pigment was originally made from a solution of copper salts with the addition of ammonium chloride and quicklime, but nearly all the lime blues now consist of ultra blue reduced with terra alba, the colour being further improved by sprinkling the mixture with a 10 per cent. solution of magnesium chloride. Lime blue is chiefly used for distemper colours.

Quantitative Estimations.

Free Sulphur.—For this determination a good method is that given by H. H. Morgan (*J. O. and C. C. Association*, October, 1919). Take a weighed quantity of the sample and extract it with methylated ether in a Soxhlet extractor for about two hours. Then distil off the ether from the flask on a water bath, place in oven for about thirty minutes, cool and weigh.

$$\frac{\text{Flask + residue} - \text{flask} \times 100}{\text{Weight taken}} = \text{free sulphur per cent.}$$

Silica and Total Sulphur.—One gram of the pigment is mixed with 25 c.c. water, 1.2 c.c. bromine added, and after about ten minutes 10 to 20 c.c. HNO_3 . The whole is then evaporated to dryness, dilute HCl added, and the liquid again evaporated to dryness. The residue is then digested for three hours with a small quantity of HCl , diluted with boiling water, and filtered. The insoluble portion is well washed with hot water, dried,

ignited, cooled and weighed = SiO_2 . The filtrate from the above is taken and the sulphuric acid precipitated with a hot solution of barium chloride, filtered, well washed, dried, ignited and weighed.

$$\text{BaSO}_4 \times 0.13738 = \text{total sulphur.}$$

Alumina and Soda.—Take 1 gram of the pigment, place in a 300 c.c. Pyrex beaker, dilute HCl added, then heat to boiling and evaporate to dryness. The residue is then taken up with dilute HCl (1 in 1), filtered, and the insoluble residue washed ten times with boiling water. The filtrate is taken, and the alumina precipitated with ammonia in slight excess, the filtrate being hot. The alumina is then filtered off, well washed, dried, ignited and weighed (Al_2O_3). The filtrate from the alumina is acidified with H_2SO_4 , 5 c.c. NH_4OH added, and the whole evaporated to small bulk, and then transferred to a previously weighed silica dish and brought to dryness, the residue being ignited and weighed.

$$\text{Na}_2\text{SO}_4 \times 0.4363 = \text{Na}_2\text{O.}$$

Thiosulphate.—Ten grams of the pigment are placed in a 500 c.c. flask and well shaken with distilled water, the liquid being made up to 500 c.c. and allowed to stand for three hours, and then filtered; 100 c.c. of the filtrate is taken and the thiosulphates determined by N/10 standard iodine solution, a freshly prepared starch solution being used as indicator. Calculate to $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

Sulphur present as Sulphates.—Take 1 gram and add dilute HCl (1 in 1), boil to expel H_2S , filtering if necessary; make the solution fairly alkaline with NH_4OH and then distinctly acid with HCl, add barium chloride, boil well, and allow to stand for thirty minutes on the hot plate, then filter. Wash the BaSO_4 precipitate ten times with hot water, dry, ignite and weigh, and calculate to sulphur trioxide and to sulphur.

$$\text{BaSO}_4 \times 0.3433 = \text{SO}_3.$$

$$\text{BaSO}_4 \times 0.1373 = \text{S.}$$

Sulphur present as Sulphide.—Subtract the sulphur present as sulphate from the total sulphur.

Chlorides.—Take 100 c.c. of the filtrate prepared for the

thiosulphate determination, and determine the chlorides by standard N/10 silver nitrate and calculate to NaCl.

$$1 \text{ c.c. AgNO}_3 = 0.005846 \text{ NaCl.}$$

Resistance to Alum.—This is an important test as regards paper-making blues. An alum solution is first made, consisting of 100 grams of potash alum dissolved in 1,000 c.c. distilled water, and then filtered 0.5 gram of ultramarine is shaken up in a test-tube with 30 c.c. of the alum solution and allowed to stand, and then shaken up again, and the rate at which decomposition takes place carefully noted. The time given is usually three hours.

The following are analyses of various ultramarines:

Sulphate Ultramarine.

							<i>Per Cent.</i>
Silica (SiO_2)	49.58
Alumina (Al_2O_3)	23.21
Sulphur (S)	9.31
Sulphur trioxide (SO_3)	2.50
Soda (Na_2O)	12.48
Moisture	2.92

100.00

Paper-Makers' Blue.

							<i>Per Cent.</i>
Silica (SiO_2)	46.21
Alumina (Al_2O_3)	21.30
Sulphur (S)	11.70
Sulphur trioxide (SO_3)	5.82
Soda (Na_2O)	9.95
Moisture	4.92

100.00

Soap-Makers' Blue.

							<i>Per Cent.</i>
Silica (SiO_2)	40.62
Alumina (Al_2O_3)	25.17
Sulphur (S)	12.96
Sulphur trioxide (SO_3)	4.92
Soda (Na_2O)	14.35
Moisture	1.98

100.00

Calico-Printers' Blue.

						Per Cent.
Silica (SiO_2)	40.72
Alumina (Al_2O_3)	24.30
Sulphur (S)	13.86
Sulphur trioxide (SO_3)	3.12
Soda (Na_2O)	15.71
Moisture	2.29
						<hr/> 100.00

Prussian Blue.—This pigment is found in various grades and qualities, as bronze blue, Chinese blue, Milori blue, Paris blue, and Berlin blue. It is a brittle pigment and hard to grind to a fine powder.

Certain varieties have a fine bronze lustre. It is fairly permanent to light and air. Prussian blue is not acted on by dilute acids, but on adding an alkali it is at once decomposed into an alkaline ferrocyanide and oxide of iron. On again adding acid the blue colour is restored. Brunswick blue is simply an extended colour of Prussian blue and barytes. Celestial blues contain still more barytes. Prussian blue requires about 50 per cent. of oil to form a stiff paste.

Quantitative Estimations.

Moisture.—Take 2 grams and place in a previously weighed weighing bottle with a good stopper—the wide form after Dr. Jankes's is the best type to use. Heat in the water oven at 98° to 100° C. for two hours. Then take out of the oven, replace the stopper, place in the desiccator to cool, and weigh. Prussian blue being a hygroscopic pigment it is better to use a weighing bottle rather than a watch glass, as in the latter event the sample should be covered by a watch glass when weighing.

Water-Soluble Matters.—According to the B.E.S.A. standard method for the estimation of soluble salts the test is carried out as follows: 1 gram of the sample is boiled for five minutes with 200 c.c. of neutral distilled water. The mixture is then cooled, and made up to 250 c.c. and filtered. Should the filtrate be coloured 0.5 c.c. of HCl is added, and then allowed to stand in a hot-water bath at 90° C. until the solution is clear, after which it is cooled and filtered again. The first 50 c.c. of the filtrate is rejected and an aliquot portion

evaporated to dryness in a silica dish which has been previously heated, cooled and weighed. The resulting residue is dried to constant weight at 95° to 98° C. A portion of the original filtrate is taken and, if coloured, pure sodium chloride to saturation point is added, and the liquid titrated with N/10 alkali, methyl red being used as indicator. This determines the acidity. If the original filtrate is not used, an allowance has to be made for the hydrochloric acid added.

Insoluble Residue.—In a pure Prussian blue or bronze blue there is practically no residue, but in the lower grades, such as Brunswick blues, barytes, china clay or other inert may be found. Take 1 gram of the pigment and place in a silica crucible, and ignite the sample under a low flame at first until any preliminary burning has ceased. Then increase the flame, but be careful not to ignite too strongly. The resulting ferric oxide residue has then added to it a few drops of HNO_3 and again ignited. This is done to insure the complete decomposition of the cyanides. Then cool, and carefully transfer the residue to a 300 c.c. beaker, add HCl and boil; then allow to stand on the hot plate for about twenty minutes, add water, and filter. Wash the insoluble well with hot water, then dry, ignite and weigh in the usual manner. This residue is nearly always BaSO_4 .

Iron Estimation.—To the filtrate add NH_4Cl and NH_4OH , boil, allow to settle and filter. Wash well. Then dissolve off the precipitate with hydrochloric acid, and make up to a known volume (250 c.c.). Take 100 c.c., reprecipitate with NH_4Cl and NH_4OH , filter, wash, dry, ignite and weigh. The result represents the combined $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$.

Now take 100 c.c. and determine the iron by the bichromate method. Subtract the total iron found from the combined iron and alumina previously estimated, the alumina being taken by difference. Test the filtrate from iron and alumina for zinc by adding $(\text{NH}_4)_2\text{S}$. It is very rarely present. If no indication of zinc is forthcoming, boil the solution well to get rid of sulphides, cool and add ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$; boil and allow to stand for a short time, then filter, dry, ignite and weigh as calcium oxide (CaO) or preferably as CaSO_4 .

Alkali Metals.—The filtrate is evaporated to dryness and carefully ignited in a platinum dish to remove salts of ammonium, and the residue dissolved in water and a few drops

of HCl added. Soluble sulphates are then precipitated with barium chloride and any excess of the reagent removed by adding ammonium carbonate and filtering off. The filtrate, which should be now free from sulphates, is evaporated to dryness, ammonium salts driven off, and the residue again treated with a few drops of HCl. This is again evaporated, preferably in a platinum dish, and gently ignited, cooled and weighed. The potassium is then determined by dissolving the residue, which now should consist of sodium and potassium chlorides, in a little HCl, and a solution of platinum chloride and a few drops of alcohol added, and the solution evaporated to a syrup consistency, dilute alcohol added, and the precipitate filtered through a Gooch crucible charged with a plug of filter-paper pulp which has been previously weighed. After the precipitate has been washed with dilute alcohol it is dried at 100° C. and weighed. $K_2PtCl_6 \times 0.3065 = KCl$. The difference between the weight of the combined residue and the potassium found = the sodium chloride present.

To obtain the percentage of Prussian blue, multiply the amount of Fe_2O_3 found by 2.8 for soda blues and 3.03 for potash blues. The foregoing analyses are sufficient for all commercial purposes. If it is desired to estimate the cyanogen the Kjeldahl-Gunning method should be employed, but it is hardly ever undertaken in a paint-works laboratory. In such a case the nitrogen obtained from a soda blue is multiplied by 3.404 and for a potash blue by 4.4. Some blues, such as Chinese blues, may contain tin salts. Should these occur or salts of manganese, they can be most conveniently sought for by qualitative means.

Cb alt Blue.—Cobalt blue is obtained in several grades and shades, being a pigment of great permanency. It is a compound of the oxides of cobalt with alumina, and occasionally phosphoric acid. It is only used by artists, and works better as a water-colour than it does in oil. Cobalt blue has a greenish tone, and when viewed by gaslight is more or less purple in shade. It is readily distinguished from imitation cobalt blues by being unaffected by acids and strong alkalies, and also by giving a sapphire blue bead with borax in the oxidising flame under the blow-pipe. In order to carry out the test proceed as follows:

Make an oval loop at the end of a piece of platinum wire which is fixed in a piece of glass rod about 4 inches long. Heat

the loop, and dip it into powdered borax, some of which will adhere to the wire. Remove the wire, and heat in the oxidising flame. The mass will froth up, owing to the disengagement of water of crystallisation, and finally give a clear bead. Take a minute trace of the cobalt pigment on the bead by bringing the heated borax in contact with the powder, and then heat strongly in the oxidising flame; a blue bead will result, characteristic of cobalt.

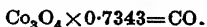
Quantitative Estimations.

Moisture.—This is estimated in the usual way.

Alumina.—Fuse 1 gram of the pigment with 14 grams sodium pyrosulphate in a platinum crucible; when fully fused, and a clear melt obtained, cool and digest with dilute HCl (1 in 1). Allow to settle, then filter, and wash the residue ten times with hot water; then dry in oven, cool, and weigh and examine the residue for SiO_2 and BaSO_4 .

Make up the filtrate to 200 c.c., add 5 grams of NH_4Cl , and heat to boiling and add dilute NH_4OH till slightly alkaline. Boil for two minutes, filter and dissolve the precipitate again with HCl, and again reprecipitate as before; filter and wash with 2 per cent. NH_4Cl solution, dry, ignite and weigh as Al_2O_3 .

Cobalt.—The filtrates from the Al_2O_3 determinations are united, 5 grams of sodium acetate added which has previously been dissolved in a little water, and H_2S passed in, when in the presence of the acetate all the cobalt will be precipitated; filter off and use the filtrate for the estimation of calcium and magnesium in the usual manner. Subtract the moisture, alumina, and other constituents from 100 and report the difference as cobalt oxide. Should phosphoric acid have been found when making a qualitative analysis, this must be removed before the alumina, calcium and magnesium are estimated. If desired, the black precipitate of cobaltus sulphide can be dissolved in aqua regia, the solution evaporated low to remove excess of acid, and then diluted with 150 c.c. of warm water. To this is added a freshly prepared hot solution of nitroso- β -naphthol in a 50 per cent. solution of acetic acid, and the solution is then left in a warm place for a few hours, then filtered through a Gooch crucible charged with asbestos pulp, washed with cold water, dried, ignited and weighed as Co_3O_4 .



Green Pigments.

Green Earth.—Green earth, terre verte or Verona green, is a natural green earth originally found in the rocks near the town of Verona, North Italy. The colour is derived from ferric oxide and ferrous oxide, the gangue being composed of silica, alumina, lime, magnesia, and potash. Various shades occur varying from dirty green to greenish-grey. It has been used as a pigment from early times, but though very permanent, it lacks body and covering power. Its chief use is as an absorbent or base in lake making, having a strong affinity for basic aniline dyestuffs. The German grades of earth exhibit the best absorbent power, fixing from 4 to 6 per cent.

Green earth should show no reaction or change of colour when treated with alkalis or acids. When a sample of fresh earth is powdered and treated with dilute hydrochloric acid, then washed and filtered, and finally dried and mixed with linseed oil, it must show no appreciable change in colour when compared in a similar manner, on a piece of clear glass, with an original specimen. A green earth which shows up a rich deep green should be viewed with suspicion. A sample should be placed in a test-tube, absolute alcohol added and well shaken, keeping the thumb over the mouth of the tube, and then allowed to settle. If the earth has been enriched by a green pigment of coal-tar origin, the alcohol will be coloured. It is also desirable to test for Prussian blue by adding caustic soda solution to another portion. The caustic will destroy the blue if present.

Brunswick Greens.—These pigments are supplied in various shades—pale, middle, deep, and extra deep. They work well both in water and oil, and have a good opacity. Brunswick green should not be mixed with pigments containing sulphur, as sulphur acts on the chrome yellow and causes a darkening. Lime also should be avoided, as lime reacts both on the blue and chrome yellow, turning the green a reddish colour. For this reason Brunswick green should not be included in pigments to be used for distempers. Sulphuretted hydrogen darkens these greens, and acids turn the pigment blue, due to the fact that the chrome yellow is dissolved. Brunswick greens are frequently sold in the reduced form, containing barytes and gypsum. A good Brunswick green should be equal in colour

and shade to the standard sample. The reduced qualities should contain only barytes, and should be free from Paris white, gypsum, etc.

When reduced with ten times its weight of zinc oxide in oil, the resultant shade must be equal to the shade of the standard sample.

Brunswick greens should not contain more than 2 per cent. of matter soluble in water.

After shaking 10 grams of the pigment with 50 c.c. of distilled water for one hour, the aqueous extract should be neutral to litmus paper.

Other greens, such as emerald-tinted greens, are similar to Brunswick greens, but have a chalky, bluish-green shade. Bronze greens are generally made by mixing in the dry state celestial blue, which is a Prussian blue mixed with barytes, lemon and orange chromes, burnt umber, and barytes. Some types of bronze greens are made from middle Brunswick green, lemon chrome and ivory black. Quaker greens are deep Brunswick greens. Middle chrome, mineral black, etc., coach greens, and Hungarian greens all have as a basis Brunswick greens, modified by the addition of tinters which alter the shade and tone of the original green.

Quantitative Estimations.

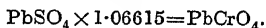
Moisture.—Take 2 grams and determine in the usual manner.

Insoluble Matter.—Take 1 gram of the pigment and boil with HCl. Take the solution down to dryness twice. This is done in order to be sure that the lead sulphate is dissolved. Then add dilute HCl (1 in 1) and filter through a previously weighed Gooch crucible charged with asbestos pulp and wash ten times with boiling water, then dry. The residue will be Prussian blue plus barytes.

Iron.—Now gently ignite the residue to decompose the blue and weigh again. The barytes is obtained by difference after the iron has been determined, which is most conveniently done by means of N/10 potassium bichromate, which has been previously described under Iron Oxides, and then multiplying the result obtained either by 2.8 for a soda blue or 3.03 for a potash blue.

Lead.—Take the filtrate from the insoluble determination and make up to 200 c.c., and having arranged matters by the

addition of a little dilute NH_4OH , so that the solution is only slightly alkaline, pass in H_2S until all the lead is precipitated as PbS . Allow the precipitate to settle, filter, and wash with H_2S water; reserve the filtrate. Place the precipitate and filter paper in a 300 c.c. beaker, add dilute HNO_3 , and boil until all the PbS has dissolved and filter; now add 10 c.c. H_2SO_4 (1 in 1) and heat until fumes of SO_3 are given off. Cool, and add about 100 c.c. water and 10 c.c. ethyl alcohol. Allow the whole to stand for about two hours and filter through a previously weighed Gooch crucible charged with asbestos pulp, and wash with water containing a little alcohol; dry, ignite at low heat, and weigh as PbSO_4 .



Chromium.—Take the alcoholic filtrate from the PbSO_4 and evaporate it nearly to dryness, and then add it to the filtrate from the PbS . Boil well to expel all H_2S and add a few drops of HNO_3 and boil for a few minutes, and precipitate the iron, aluminium and chromium hydroxides with NH_4OH . Then filter and wash. Dissolve the precipitate with HCl and make up the solution in 250 c.c. flask. Take 50 c.c., precipitate with NH_4OH , wash, dry and weigh. Take another 50 c.c. and add sodium peroxide (Na_2O_2) until the iron hydroxide has turned reddish-brown, dilute with 50 c.c. water, filter, wash and determine the iron as Fe_2O_3 . Take the filtrate from the iron, add HNO_3 and then add NH_4OH , filter, wash and weigh as Al_2O_3 . Take 50 c.c. from the 250 c.c. flask and determine the chromium as outlined under lead chromate. The amount of CrO found $\times 3.2300 = \text{PbCrO}_4$. If calcium and magnesium require estimating, they can be determined in the filtrate from the above hydroxide in the usual manner.

It should be mentioned that a pure Brunswick green should consist of Prussian blue and lead chrome only, but most of them contain barytes. In some cases the pigment is produced by precipitation methods, while in other cases mechanical mixing is resorted to. For this reason a microscopical examination should be made at the outset before starting the analysis. A green of the former class will most likely show green and blue particles, while one mechanically blended, frequently many yellow and blue particles, together with a certain amount of green ones. In most cases the insoluble matter, iron and lead

are alone determined when carrying out a works examination, but, as will be seen, the chromate under the scheme given is checked twice, both from the lead sulphate determination and when the chromium is estimated.

Zinc Green.—The permanency of zinc green is much greater than that of Brunswick greens. These greens are composed of Prussian blue, zinc chrome and barytes, and are manufactured on similar lines to Brunswick greens.

Zinc greens are not affected by sulphuretted hydrogen, and can therefore be used with advantage both for outside and inside paints, but they are unsuitable for lime colours.

Zinc greens originally were mixtures of zinc chrome and Prussian blue, or in some cases ultra blue. More recently they may be mixtures of monastral blue (copper phthalocyanine) and zinc chrome. It is not often that these greens are examined quantitatively, but if Prussian blue and zinc chrome have been used they can be determined as described under Brunswick Green as regards insoluble matters, iron, etc.; and the zinc and chromium as given under Chromes.

Qualitative tests will show the presence of ultra blue by the blue being discharged on boiling with dilute HCl, and the evolution of H_2S turning lead acetate paper black; the monastral blue by heating 1 gram of the pigment in a crucible to destroy the organic matter, taking up the residue with dilute HCl, filtering and testing with NH_4OH , and obtaining a blue precipitate of copper hydroxide readily soluble in the reagent to a deep blue solution.

Green Oxides of Chromium.—There are two green oxides of chromium pigments, one an opaque green, an anhydrous oxide, Cr_2O_3 , and Guignet's green, $Cr_2O_3 \cdot 2H_2O$, which is a green pigment having a slightly yellowish tone. It has a fair body, and is quite permanent. It can be mixed with all other pigments without affecting them in any way. When treated with hydrochloric acid it should not impart any yellow colour; a yellow colour would indicate the presence of chrome yellow. When boiled with caustic soda the pigment should remain unchanged. Should the pigment be suspected of being adulterated with Brunswick green, add hydrochloric acid and then ferric chloride; a blue precipitate would indicate Prussian blue. When mixed with zinc chrome the resulting pigment is known as Victoria or Nuremberg green.

Quantitative Estimations.

Green chromic oxide prepared by the reduction of chromates and Guignet's green made by heating a mixture of potassium or sodium dichromate and boric acid are not often analysed by the paint-works chemist, as a qualitative analysis will usually furnish the necessary information as to whether any other green pigment is present. If quantitative estimations are required, these pigments are usually examined for the following:

Moisture.—Take 1 gram and dry to constant weight.

Combined Water.—Heat 1 gram in a covered porcelain or platinum crucible over a Bunsen burner not too strongly at first, and finally over the blowpipe to constant weight.

Total Chromium.—One gram of Guignet's green which has been previously ignited is well mixed with Na_2O_2 in a nickel crucible provided with a lid. The crucible is heated until the mixture has gone to complete fusion, which may take from fifteen to twenty minutes. The crucible is then cooled, another gram of Na_2O_2 is added, and the whole fused again for about five minutes. After cooling, the crucible is placed in an evaporating dish, 150 c.c. water added, and the melt extracted by boiling. The crucible is then removed by a pair of crucible tongs and well washed with water, 5 grams of solid ammonium carbonate added (this assists filtration), and the mixture is boiled, diluted with about 50 c.c. water and filtered, and should there be any insoluble residue this is well washed and estimated. The filtrate containing the chromium is then made up to 200 c.c., and 50 c.c. taken and placed in a conical flask, N/10 ferrous ammonium sulphate added from a burette until the colour of the solution turns green, when a further 2 c.c. is added and the excess is titrated with N/10 potassium permanganate.

1 c.c. potassium permanganate = $0.00253 \text{ Cr}_2\text{O}_3$.

Red Pigments.

Iron Oxides.—Red pigments as used by the paint manufacturer consist of natural red oxides of iron, Turkey red, Venetian red, red ochres, Tuscan reds, red lead, vermilion, and vermilionettes. Natural red oxides of iron are prepared by levigation and grinding. Artificially prepared oxides are made by roasting iron sulphate. The finest and best shades of natural

earth colours come from Spain and the Persian Gulf. Red oxides vary in shade from a pale red to a dark purple, possessing great covering power, and also good staining power. These properties do not depend so much on the purity and percentage of iron oxide as on physical conditions. Red oxides mix well with all pigments without affecting them and are very permanent. The colour strength of a Venetian red which has been lightly calcined is usually greater than an Indian red which has undergone strong calcination. When applied as paint to metal surfaces, a natural oxide is to be preferred to one which has been artificially manufactured. Venetian reds are sometimes made by grinding a very bright natural oxide with terra alba.

A good natural Spanish oxide will contain about 84 per cent. of iron oxide (Fe_2O_3). Turkey red oxides range from about 90 to 95 per cent.; Indian reds 86 to 98 per cent. Red oxides such as Tuscan reds are frequently brightened by the addition of an organic dye such as alizarine. In order to determine whether an organic dye has been added, the sample is heated to redness, when a loss of brightness will take place if organic matter is present. Red oxides are tested for colour and staining power in the usual manner.

The percentage of oil to make a stiff paste is on the average as follows:

							<i>Per Cent.</i>
Oxides of iron	23-25
Tuscan red	23-26
Indian red	20-21
Venetian red	23-25

Red Lead.—This pigment has the formula Pb_3O_4 , and was formerly known under the name of minium. Like all lead pigments it is easily affected by sulphuretted hydrogen, turning black, and when exposed to the direct action of the sun it has a tendency to bleach, due to loss of oxygen and to returning partly to the monoxide state. It has a fair opacity, and has a strong drying action on linseed oil, but the staining power is poor. When boiled with dilute nitric acid, and a little oxalic acid is added, the pigment should completely dissolve. The oil absorption is about 12 per cent. Specific gravity is 8.681.

Quantitative Estimations.

Moisture.—This is determined in the usual manner.

Organic Colouring Matters.—Take 2 grams and add 25 c.c. 95 per cent. ethyl alcohol and boil, then allow to settle. Decant off the supernatant liquid, add 25 c.c. water and boil again; decant off the water after the residue has settled and add dilute NH_4OH (1 in 10). Take a fresh portion of the sample and shake up with chloroform. Should the alcohol, water, dilute ammonia, or chloroform be coloured, then an organic colouring matter is indicated.

Insoluble Residue and Total Lead.—Take 1 gram of the sample and add 15 c.c. dilute HNO_3 (1 in 1) and H_2O_2 to dissolve the lead peroxide (PbO_2) on warming. Should any insoluble matter appear, if in very small amount it is most likely silica, but should it be considerable it might be BaSO_4 added intentionally. Add 25 c.c. water and boil, allow to settle, filter and wash well with boiling water, then dry and weigh, and examine the residue. To the filtrate from the insoluble add 20 c.c. H_2SO_4 and evaporate till SO_3 fumes come off, then cool, add 10 c.c. water and 10 c.c. ethyl alcohol, and allow the solution to stand three hours, then filter through a Gooch crucible charged with asbestos pulp, washing with 10 per cent. alcohol solution, dry, ignite at low heat, and weigh as PbSO_4 .

$$\text{PbSO}_4 \times 0.6829 = \text{Pb.}$$

$$\text{PbSO}_4 \times 0.7360 = \text{PbO.}$$

Determination of PbO_2 and Pb_2O_4 (True Red Lead) (after Scott and Furman).—Take 1 gram, place in 200 c.c. beaker and add 15 c.c. HNO_3 (made from 110 c.c. HNO_3 , sp. gr. 1.42, and water 100 c.c.). Stir the mixture with a glass rod until all traces of red colour have disappeared. Now add from a burette 10 c.c. of dilute hydrogen dioxide (1 part of the H_2O_2 3 per cent. strength and 3.5 parts of water).

Now add 50 c.c. hot water and stir until all the lead dioxide has gone into solution. If all has not gone up, continue stirring and at the same time warm gently the solution. Now dilute with hot water to 250 c.c. and titrate with N/10 potassium permanganate having an iron value of 0.0055 to a faint pink. Take another beaker and add 15 c.c. of the above nitric acid solution and 10 c.c. of hydrogen dioxide, dilute to 250 c.c. with hot water, and titrate again to a faint pink with potassium

permanganate. The difference between the number of c.c. of KMnO_4 required for the blank titration and the amount required for the red lead titration will be the amount required for the H_2O_2 which has been reacted on by the red lead. The difference between these two amounts multiplied by 3.058 gives the percentage of red lead present, and the difference multiplied by 1.067 gives the percentage of PbO_2 .

Vermilion.—This pigment is mercuric sulphide (HgS). There are two varieties, pale and dark. Chinese vermilion has a fine crimson shade. It has been stated that vermilion prepared from native cinnabar is more permanent than that made artificially. A crimson vermilion is generally more transparent than the pale or finer ones, the crystals of a deep crimson vermilion being coarser.

Metallic mercury, iron, and free sulphur are best detected by dissolving the pigment in potassium mono-sulphide solution (1:1). In this solution vermilion dissolves fairly readily. If metallic mercury is present, it will settle after a time at the bottom of the beaker as a grey powder, and free sulphur will impart a yellow coloration to the solution. Should iron be present, ferrous sulphide will form, which will settle out, leaving a clear solution.

Vermilion is unaffected by dilute acids and alkalies. Both the capacity and staining power are good. What is known as American vermilion is really a scarlet lead chromate, also known as Chinese red, Persian red, and Imperial scarlet. American vermilion requires about 20 to 22 per cent. of oil to make a paste, while true vermilion takes from 16 to 19 per cent.

Vermilionettes.—These pigments are also known as royal reds and signal reds. They are pigments consisting of an aniline dye (eosin or other coal tar red), along with red lead, orange lead, barytes, or terra alba. Most of them are not very permanent to light.

They may consist of such combinations as :

							Per Cent.
Organic colour	3
Lead oxide	97

or—

							Per Cent.
Para red	10
Barytes	90

Or again-

						<i>Per Cent.</i>
Organic dyestuff	40
Lead oxide	10
Barytes	50

These are typical examples.

When ignited in a silica crucible over a Bunsen flame, pure Chinese vermilion volatilises away, but in the case of vermilionettes the coal tar pigment is destroyed, the lead base being left. If vermilionettes are boiled with a mixture of alcohol and ammonia, a coloured filtrate will be produced, eosin imparting a green fluorescence. Lead compounds, barytes, etc., can be tested for by boiling the pigment with nitric acid, then diluting with water, adding oxalic acid, and if lead only is present, a clear solution will result. Should barytes be present, this will be left as a white residue, which can be confirmed by the flame test.

Organic Toners and Lake Colours.

Lake colours are largely used for the manufacture of printing inks and may be divided into the following groups:

- (I.) Acid dyestuffs precipitated with barium chloride.
- (II.) Basic dyestuffs precipitated on green earth.
- (III.) Resorcin dyestuffs precipitated with lead acetate.
- (IV.) Diazo dyestuffs.
- (V.) Mordant dyestuffs precipitated on alumina.

The chief bases used are barytes (blanc fixe), alumina, terra alba, china clay, green earth, red lead, and zinc oxide.

When considering lake colours it is interesting to note that the coarser the nature of the base, the fuller and deeper is the resulting pigment, whereas the finer the base the weaker it looks in dry powder form, but nearly always gives stronger reductions, and the more transparent the base the greater the staining power.

For the analysis of the base place a small quantity of the finely powdered lake colour in a silica crucible and heat over a Bunsen burner. Burn off the organic dyestuff and treat the residue in a beaker with hydrochloric acid and boil. Add distilled water, and filter off the residue and wash it well with boiling distilled water. Should barytes be present, test the

colour differences, if any, noted; where an arc light is not available, compare in a good bright north light.

Strength.—Two one-hundredths of a gram of carbon is taken and 2 grams of zinc oxide and transferred to a glass slab or lithographic stone, and 2 $\frac{7}{10}$ c.c. of water-white mineral oil added from a burette, and the two pigments well worked together with a spatula. (In carrying out this test the author has found that water-white medicinal paraffin works very well.) The mixture is then mullied with the weighed muller fifty times as described before, and is then gathered together as previously described and the process repeated, and the mulling and gathering together is repeated until the number of mulling strokes has reached 200. The same procedure is applied to the standard. The two samples are then gathered up, placed on a clean microscopical slide as before, and any difference in tinting strength noted. To obtain a quantitative result, the stronger of the two pigments is further reduced by adding increased amounts of zinc oxide until the ratio is reached at which the strength of the weaker samples exactly matches the stronger. For example, if it is necessary to add 3 grams of zinc oxide with 0.02 gram of the carbon black of the stronger pigment, then the stronger black is 50 per cent. stronger than the weaker one.

Moisture.—One gram of the sample is dried for one hour at 105° C., and is then cooled and reweighed in the usual manner.

Ash.—One gram is placed in a Tard porcelain crucible and heated with the crucible lid off at 1,700° F. (approx. 926.5° C.) in an electric furnace or a good gas muffle until all the carbon has been burnt away and until repeated cooling in a desiccator and weighing shows constant weight.

Acetone Extract.—This is best done in a Soxhlet extractor, using a tared flask 250 c.c. The extraction thimble is filled with a weighed amount of the carbon to within 1 inch of the top, covered with glass wool, and then extracted for at least six hours with 210 c.c. redistilled acetone, the extraction preferably giving from two to four syphoning actions per hour. The extract is then carefully distilled off and the drying completed in an oven at 70° C.

$$\frac{\text{Increase in weight of flask} \times 100}{\text{Weight of carbon taken}} = \text{acetone extract.}$$

Examination of Mixed Paints.

In the qualitative examination of mixed paints, it is first necessary to remove the oil and thinners, or, in the case of paste pigments, the oil.

In the *Journal of Industrial and Engineering Chemistry*, February, 1909, a method of oil extraction is described in a paper by Herty, Stem, and Orr, using carbon tetrachloride. Though originally designed for the estimation of oils in feeding-cakes and meals, it is a very useful method for preparing the pigments for analysis from stiff and ready-mixed paints. Carbon tetrachloride has a very good solvent power for oils and fats, coupled with a relatively high boiling-point and low heat of vaporisation. The method of procedure is as follows: 20 to 40 grams of the paint are taken and transferred to an Erlenmeyer flask which is placed on a water-bath previously heated to 60°C . ($=140^{\circ}\text{F}$). The flask is left on the bath for about five minutes, after which 100 c.c. of pure carbon tetrachloride are poured in and the whole well mixed. The flask is then returned to the water-bath until the surface of the water is above the carbon tetrachloride, and the flask is kept at 60°C . for forty-five to sixty minutes. The solvent is then filtered off, and the pigment on the filter washed six times with small quantities of carbon tetrachloride. The pigment will now be found to be practically free from oil, and can be dried. It is then preserved—after being crushed up in a mortar—in a stoppered bottle.

The method of examining extracted pigments is similar to that given in *Paint Manufacture* for March, 1935, and is carried out as follows: Take about 2 grams and add acetic acid slowly to the pigment until all carbonates are decomposed (noting whether any hydrogen sulphide is evolved); then add a large excess of acid ammonium acetate solution; boil, filter, and test the filtrate for metals other than lead and zinc. The absence of calcium in this filtrate indicates that the extending pigments contain no calcium carbonate or calcium sulphate; the absence of barium indicates that the extending pigments contain no barium carbonate. Wash the insoluble matter in acid ammonium acetate solution with another portion of this solution, and finally with hot water. This insoluble matter is dried, ignited, and tested for silicious matter, barium sulphate,

and titanium compounds. To test for the latter, place a small amount of the insoluble matter, or of the original pigment (0.5 gram), in a 250 c.c. Pyrex glass beaker, and add 20 c.c. H_2SO_4 and 7 to 8 grams of ammonium sulphate. Mix well, and boil for a few minutes. A residue denotes the presence of SiO_2 or silicious matter. Cool the solution, dilute with 100 c.c. water, heat to boiling, settle, filter, and wash with 5 per cent. hot H_2SO_4 until free from titanium. The residue may be tested for lead, barium, and silica. Add hydrogen peroxide to a small portion of the filtrate; a clear orange-yellow colour indicates the presence of titanium. Boil another portion of the filtrate with zinc; a pale blue or violet coloration indicates titanium.

Treat another portion (1 gram) of the pigment with 20 c.c. HCl (1:1) and note whether any H_2S is evolved; boil the solution for about five minutes, add 25 c.c. of hot water, filter, and wash well with hot water. Render a portion of the filtrate alkaline with NH_4OH , acidify with HCl , and add barium chloride solution; a white precipitate of barium sulphate indicates the presence of a soluble sulphate. To another portion of the filtrate add a little H_2SO_4 ; a white precipitate indicates the presence of lead, soluble barium or both (some calcium sulphate may also separate); filter, wash well to remove free acid, and treat the precipitate with a few drops of potassium iodide solution; a yellow precipitate of Pb_2 will indicate lead. To another portion of the original filtrate add NH_4OH until alkaline; render slightly acid with acetic acid, boil, and add $\text{K}_2\text{Cr}_2\text{O}_7$ solution; a yellow to orange-yellow precipitate will indicate lead, soluble barium or both. To another portion of the original filtrate add a few drops of potassium ferrocyanide solution; a bluish-white precipitate will indicate zinc. Pass into the remaining portion of the original filtrate H_2S for five to ten minutes; add an equal amount of water and again pass H_2S into the solution; filter, wash with H_2S water, and digest the precipitate with ammonium polysulphide; filter, acidify the filtrate with HCl and warm; the presence of antimony is indicated by the separation of an orange precipitate. The filtrate from the H_2S precipitate may be tested for barium, calcium, and magnesium in the usual manner.

Quantitative Scheme for White Paint.—For mixtures containing basic lead carbonate, basic lead sulphate, zinc oxide,

carbonates and sulphates of calcium (*i.e.*, whiting and gypsum), and carbonates and sulphates of magnesium.

(1) Open the container and stir well for fifteen to twenty minutes until the whole is perfectly mixed up. Make a cap with half a single-walled extraction thimble, and place on a double-walled thimble, and dry and weigh the two together.

(2) Fill two-thirds full with the paint and weigh again. Difference in weight is the amount of paint taken for analysis.

(3) Extract all day (eight hours), using a mixture of:

1 part ether,
1 part acetone,
1 part benzene,

or with carbon tetrachloride alone.

When the paint has been fully extracted, take out the thimble and dry in the electric oven. Distil off solvent and examine the oil.

Dry Pigment.—Estimate:

- (a) Lead soluble in acid ammonium acetate. Calculate to total Pb.
- (b) Lead soluble in acetic acid. Calculate to total Pb.
- (c) Zinc. Calculate to total ZnO.
- (d) Carbon dioxide.
- (e) Ca soluble in a mixture of 9 parts 95 per cent. alcohol and 1 part concentrated HNO_3 . Calculate to CaCO_3 .
- (f) Total Ca. Calculate to CaO.
- (g) Total Mg. Calculate to MgO.
- (h) Total SO_3 .

Calculations:

- (1) Total Pb (a)—white Pb plus PbO in (b) . . . PbSO_4 .
- (2) Calculate Ca found in (e) to CaCO_3 .
- (3) Total CaO (f)—CaO from (e) . . . CaO left for CaSO_4 .
- (4) Total SO_3 (h)— SO_3 from (1) and (3) . . . SO_3 left for MgSO_4 .
- (5) Total MgO (g)—MgO from MgSO_4 (4) . . . MgO left for MgCO_3 .
- (6) Total CO_2 — CO_2 from MgCO_3 CaCO_3 . . . CO_2 left for the white lead.
- (7) Total Pb—Pb of white lead and PbSO_4 . . . Pb left for PbO.
- (8) Zinc found in (c) expressed as ZnO.

Note.—The insolubility of calcium sulphate in a mixture of 9 parts of alcohol and 1 part of nitric acid forms the basis of the above calculation.

SECTION III

OTHER TESTS

(1) Oils and Turpentine.

The following are various types of linseed oils:

<i>Source.</i>	<i>Colour.</i>	<i>Specific Gravity.</i>	<i>Iodine Value</i>
Calcutta	Pale	0.932	180-186
Bombay	Straw	0.932	180-185
La Plata	Straw	0.931	170-180
Baltic	Brown green	0.936	170-195
Belgium	Dark straw	0.936	170-175

Linseed Oil.—According to Dr. H. A. Gardner the constants for raw, refined, and boiled linseed oils are as follows:

Raw Linseed Oil.

		<i>Max.</i>	<i>Min.</i>
Loss on heating at 105°-110° C.	..	0.2 per cent.	—
Foots by volume	2.0 "	—
Specific gravity at 15.5° C.	0.936 "	0.932
Acid number	6.0	—
Saponification number	195.0	189.0
Unsaponifiable matter	1.5 per cent.	—
Iodine value (Hanus)	—	170

Colour not darker than a freshly-prepared solution of 1 gram potassium bichromate in 100 c.c. pure strong (1.84 specific gravity) sulphuric acid.

Refined Linseed Oil.

		<i>Max.</i>	<i>Min.</i>
Loss on heating 105°-110° C.	0.2 per cent.	—
Foots by volume	2.0 "	—
Specific gravity at 15.5° C.	0.936	0.932
Acid number (acid refined oil)	9.0	3.0
Acid number (alkali refined oil)	3.0	—
Saponification number	195.0	189.0
Unsaponifiable matter	1.5 per cent.	—
Iodine value (Hanus)	—	170

Boiled Linseed Oil.

	<i>Max.</i>	<i>Min.</i>
Loss on heating at 105°-110° C.	0.2 per cent.	—
Specific gravity at 15.5° C. ..	0.945	0.937
Acid number	8.0	—
Saponification number ..	195.0	189.0
Unsaponifiable matter ..	1.5 per cent.	—
Iodine number (Hanus) ..	—	168
Ash	0.7 per cent.	0.20 per cent.
Manganese	—	0.03 „
Lead	—	0.10 „
Time of drying on glass (hours)	20	

Linseed oil is not often adulterated, but should it contain rosin oil this can be detected by the Liebermann-Storch test, which is performed as follows: Gently warm in a porcelain dish a small quantity of the suspected oil with an equal volume of pure acetic anhydride, and add 1 drop of sulphuric acid, made by mixing 34.7 c.c. pure sulphuric acid with 35.7 c.c. distilled water. Should rosin be present, a rapidly fading violet coloration will be produced. Should mineral oil be suspected, take a large test-tube and half fill it with 90 per cent. alcohol, add a small piece of caustic potash, and warm till dissolved. Now add 3 or 4 drops of the linseed oil and boil for five minutes, and then add distilled water; should mineral oil be present, a milky solution will result.

To distinguish between ordinary linseed oil and boiled oil, shake up in a test-tube 12 c.c. of the oil with 6 c.c. of glycerine-lead mixture, which is made by mixing 1 c.c. of 20 per cent. ammonia with 5 c.c. of a solution of lead acetate. The latter solution is made by dissolving 100 grams of lead acetate in 150 c.c. distilled water, and then add 32 grams of glycerine. The test-tube is placed for three minutes in boiling water. Boiled oil will form a thick pasty emulsion, while ordinary linseed oil separates into two layers, the bottom one of which consists of clear water. By this method pure linseed oil can be distinguished from an oil which may have mixed with it as much as 25 per cent. of boiled oil, and the process is correct for all boiled oils with driers, but not for boiled oils (blown oils) without driers.

To distinguish blown oils from ordinary linseed oil a test devised by Morpurgo is employed, and is as follows:

First saponify the oil with potash (KOH) by boiling a small quantity of the oil in a flask with alcoholic caustic potash solution. The resulting soap is dissolved in water, and the clear solution treated with common salt (NaCl) until no more soap separates out. If after filtration the filtrate is made strongly acid with glacial acetic acid, a turbidity shows the oil was either a blown or boiled oil, while the filtrate from a raw oil will remain clear.

Specific Gravity.—This is best determined by means of the Westphal balance. In this instrument a glass plummet suspended by a piece of thin platinum wire is attached to the end of a graduated lever, and on immersing the plummet in a liquid it loses a certain weight. This equilibrium is restored by hanging on the lever a series of riders, which are so adjusted in weight as to make the reading of their values very simple. The plummet displaces exactly 10 c.c. of liquid, and hence the weight required to restore equilibrium equals that of 10 c.c. of the fluid of which the density is required. The following are the specific gravities of Baltic linseed oil under various forms of treatment:

Raw oil	0.9362
Acid, refined	0.9318
Alkali, refined	0.9317
Boiled oil	0.9502
Blown oil	0.9950

Acid Value.—This represents the number of milligrams of potassium hydroxide required to neutralise the free fatty acids in 1 gram of an oil or fat. The mineral acid value represents the number of milligrams of potassium hydroxide required to neutralise the free mineral acid in 1 gram of oil or fat. Mineral acids are generally expressed as hydrochloric acid or sulphuric acid; fatty acids as oleic or stearic acids. In order to make the determination, weigh out any convenient quantity of the oil (say 3.254 grams) and place in a 200 c.c. flask, and add 50 c.c. of a mixture of alcohol and benzene which has been previously neutralised with N/10 KOH, using phenolphthalein as the indicator. Heat the flask in a water bath, having connected the flask to a reflux condenser, in order to dissolve the fatty acids. The flask is so heated for about fifteen minutes, then disconnected and cooled, and the contents titrated with N/10

KOH, using phenolphthalein as indicator. The standard solution must be added drop by drop at the end, in order to obtain a permanent pink end point.

- 1 c.c. N/10 KOH=0.0284 gram stearic acid,
- 1 c.c. N/10 KOH=0.0256 gram palmitic acid,
- 1 c.c. N/10 KOH=0.0282 gram oleic acid,

assuming 3.5 c.c. of the standard alkali solution has been used.

$$\frac{3.5 \times 0.0282 \times 100}{3.254} = 3.03 \text{ oleic acid.}$$

An excellent method to determine the acidity of dark oils when the end reaction is sometimes difficult to see, especially in the case of boiled oils, is as follows:

Take 3 grams of the sample and place in a wide-mouthed boiling flask, with a mixture of 25 c.c. absolute alcohol and 25 c.c. benzine and redux in a water bath for half an hour, then cool. Transfer the whole to a 400 c.c. Philips flask, wash out the boiling flask with alcohol and benzine mixture, and transfer the washings to the Philips flask. Now add 50 c.c. neutralised solution of NaCl which has been cooled after being saturated with NaCl when hot, then add 15 to 20 grams powdered NaCl and finally 20 drops of phenolphthalein. Now titrate the mixture with N/5 aqueous KOH; a perfect end point will be obtained, but, if overshoot, titrate back with N/5 H₂SO₄.

The calculation is as follows:

$$\frac{\text{C.c. taken of N/5 KOH} \times 11.2}{\text{Weight of sample}} = \text{acid value.}$$

Iodine Value.—There are three methods of determining the iodine value—viz., Wijs, Hanus, and Hübel—but the Wijs method is most frequently used, and will be described here; but whichever method is employed, it should always be stated after the iodine number figures. The iodine value represents the iodine absorbed by the unsaturated fatty acids in an oil or fat. The weight of iodine absorbed by a weighed quantity of the oil, generally about 0.1 gram of oil, is calculated on the basis of 100 grams of the oil or fat, hence it is the percentage of iodine absorbed. The amount of sample taken depends on the nature of the oil under examination. For a non-drying oil with an iodine value of say 0.30 take 1 gram, for an oil with an approximate value between 30 to 50 take 0.5 gram, with an

oil 50 to 100 value 0.3 gram, and for an oil 100 to 150 value 0.2 gram, while for oils like linseed, china-wood oil, etc., 0.15 gram of the sample.

The Wijs solution is prepared as follows:

Dissolve 7.8 grams of iodine trichloride and 8.2 grams of iodine separately in pure glacial acetic acid. The two solutions are mixed and made up to 1,000 c.c. with glacial acetic acid, and carefully stored in a stoppered dark brown or yellow glass Winchester bottle. The oil, or in the case of a fat (previously melted), is weighed into a small glass or silica capsule of 1 to 2 c.c. capacity, and placed in a 250 c.c. dry and clean flask having a ground glass stopper. Next 10 c.c. of chloroform or carbon tetrachloride are added, and then followed by 25 c.c. of the iodine reagent, which is added from a 25 c.c. pipette. The flask is then closed with the stopper, shaken to get the contents well mixed, and placed in a dark cupboard for one hour for oils having an iodine value below 150, and for three hours for oils over 150. At the end of the respective periods, according to the nature of the sample under test, 20 c.c. of potassium iodide solution (freshly made) is added, and 100 c.c. distilled water, and the excess of the iodine titrated with N/10 or N/50 sodium thiosulphate. The addition of the sodium thiosulphate causes the solution to turn a pale yellow in colour. Now add 3 c.c. freshly prepared starch solution, and continue the titration carefully until the blue colour due to the starch solution has just disappeared. A blank test must be carried out exactly in the same way minus the sample of oil. The calculation is as follows:

If a represents the c.c. used of N/10 sodium thiosulphate in the actual test, b the blank, and X the amount of sample taken, then

$$\frac{b - a \times 1.269 \times 100}{X} = \text{iodine value.}$$

Example.—Blank test took 49.2 c.c. sodium thiosulphate, a took 33.4 c.c., and amount of oil taken 0.312 grams:

$$\frac{49.2 - 33.4 \times 1.269 \times 100}{0.312} = 64.29.$$

Saponification Value.—This represents the number of milligrams of potassium hydroxide required to saponify—in other

words, convert into soap—the total fatty acids in 1 gram of an oil or fat. Sometimes the term “saponification equivalent” will appear, and is the number of grams of an oil or fat saponified by 56.1 grams of potassium hydroxide.

To carry out the saponification value, the standard solutions required are N/5 HCl and N/5 alcoholic solution of KOH. About 2 grams of the sample are weighed out into a 200 c.c. alkali-resisting glass flask, and 25 c.c. of the standard alcoholic KOH added, and in order to prevent any bumping when boiling, a few pieces of pipe-clay or pumice should be added. The flask is connected with a reflux condenser and boiled for thirty minutes, after which the excess alkali is titrated with N/5 HCl in the presence of phenolphthalein. A blank test must be carried out under exactly the same conditions to obtain the strength of the standard KOH. If A represents the c.c. used in the blank, and B those used in the actual test, and W the weight of sample taken, then

$$\frac{A - B \times 28.05}{W} = \text{saponification number.}$$

Viscosity.—There are two methods of determining viscosity—viz., by the capillary tube and the falling sphere method—but for the determination of linseed and other seed oils the capillary tube is used, while thick blown oils, stand oils, etc., are determined usually by the latter method.

The capillary tube consists of a U-tube with a bulb on each arm, the bottom of the upper or left-hand bulb being at a higher level than the top of the lower bulb. The sample to be tested is run in so that the level is at the graduation A (see illustration) and must be at the temperature necessary for the determination. The oil is then carefully drawn up to the mark B, and the time required for the oil to run down to the mark C noted. If the data relating to the U-tube are known, then the viscosity in poises can be ascertained from the following formula:

$$\frac{8LV}{\text{time}} = \eta \text{ (poises).}$$

It is not necessary, however, to apply this formula to each viscosity determination, as the tubes can be supplied already standardised with a liquid, usually a mixture of glycerine and

water, so that the viscosity is the product of the factor plus the specific gravity plus the time of flow in seconds, and the factor, etc., can be obtained from the apparatus suppliers. Standard viscometers are supplied as No. 0, 1, 2, 3, 4, with certificates and factors.

There are four standard (B.S.I.) tubes in use at the present time, and the cost of a set of tubes with certificates is approximately £5.

No. 1 for liquids between 0.9-7.2 centipoises.

No. 2 for liquids between 5.4-43 centipoises.

No. 3 for liquids between 32-260 centipoises or 2.6 poises.

No. 4 for liquids between 1.900-1.500 centipoises or 15 poises.

In the falling-ball method a small metal (steel) ball such as is used for ball bearings is allowed to sink through a column of liquid which is of known height, recording the fall in seconds, and is an instrument suitable for liquids having a viscosity not less than 10 poises. The tubes are 32 mm. bore, 250 mm. long, with two marks and sets of steel balls $\frac{1}{16}$, $\frac{3}{32}$ and $\frac{1}{8}$ inch, and a thermometer 5° to 50° in 1° . The whole is contained in a glass jar with a teak cap and foot with levelling screws, funnel, syphon tube and stirrer. In all determinations the control of the temperature is very important. If the temperature rises the ball will fall quicker, and *vice versa*. Some oils such as castor oil thin rapidly under increase of temperature, much more so than other vegetable oils such as linseed, perilla, etc. The viscosity is calculated from the following formula:

$$\frac{td^2(\sigma - p)g}{18S(1 \times 2.4d)(1 \times \frac{5d}{3h})} = \eta.$$

(1) t = time in seconds for the ball to fall S.C.M.S.

(2) g = 981 CM/sec².

(3) σ = density of ball in gms./c.c.

(4) p = specific gravity of the oil or other liquid.

(5) D = diameter of tube in C.M.

(6) h = height of liquid in C.M.S.

(7) d = diameter of ball in C.M.S.

Specification for the determination of viscosity in absolute units, British Standards Institution, 28, Victoria Street, London, S.W.1.

Apart from the standard viscosity methods described, the following method, though primarily intended for lubricating oils, can be used for paint oils and varnishes as a general check on viscosities. A 100 c.c. long bulb pipette is required, and regulated to hold exactly 100 c.c. to the bottom of the bulb. The size of the aperture at the bottom is then made so that 100 c.c. of water at 100° F. will run out of the pipette down to the bottom of the bulb in thirty-four seconds. The oil to be tested is uniformly heated and then sucked up into the pipette

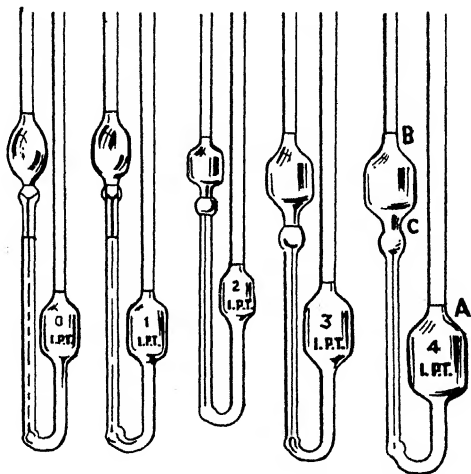


FIG. 4.—STANDARD VISCOMETER TUBES.

to the mark. The time taken by the oil in running down to the bottom of the bulb is then noted. The room temperature affects the result slightly, but if kept at about 65° F. very uniform results are obtained. The whole apparatus is improved if a tap is inserted in the tube of the pipette above the bulb. It is inexpensive and a useful viscosity guide for general works purposes.

China-Wood Oil or Tung Oil.—According to Dr. H. A. Gardner, the following represents the maximum and minimum figure for raw tung oil:

	<i>Maximum.</i>	<i>Minimum.</i>
Specific gravity at 15.5° C.	0.943	0.940
Acid number	8.0	—
Saponification number	195.0	190
Unsaponifiable matter	0.75 per cent.	—
Refractive index at 25° C.	1.520	1.5165
Iodine value (Wijs) ..	—	163
Heating test (minutes)	12	

Heating Test.—The accompanying figure represents the apparatus used for carrying out this test (Fig. 5).

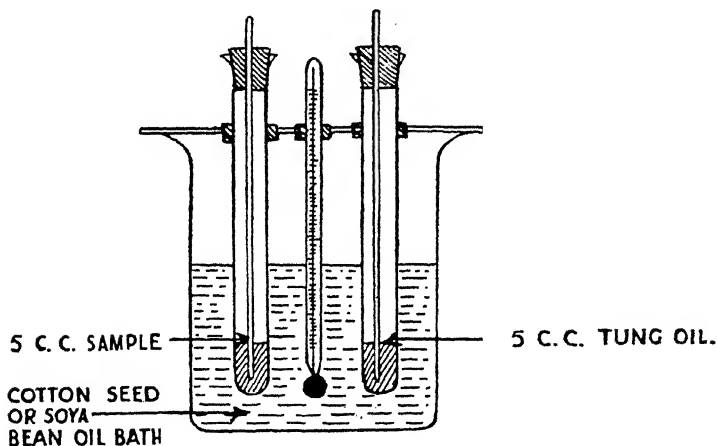


FIG. 5.—APPARATUS FOR CARRYING OUT HEATING TEST ON TUNG OIL.

The two test-tubes for containing the oil should be 15 cm. by 16 cm., and near the bottom of the tubes should be a mark indicating 5 c.c. The tubes are closed by perforated corks, each having a perforated glass rod 3 mm. in diameter which can move freely. These tubes are supported by a piece of wood with three holes, the two side-holes being for the test-tubes and the middle one for a thermometer graduated from 210° to 310° C. The tubes stand in an 800 c.c. beaker which is filled with cotton-seed oil. The tubes having been filled in each case with 5 c.c. china-wood oil, one being the sample and the other the standard of known value, the beaker is heated up to 293°, rising very slowly. Place the tubes in the beaker so that the

bottom of the thermometer bulb is level with the bottom of each tube, and 1.5 cm. from the bottom of the beaker. Now note the time. Remove the source of heat for forty-five seconds, and then reheat. Before two minutes the temperature of the bath will have fallen to 282°. At this point keep the temperature as level as possible.

After the samples have been in the beaker for nine minutes, begin raising the glass rods every fifteen seconds, and note the time when each sample becomes firmly set. The jellying or setting takes place in a few seconds from fluidity.

The following test is at times found useful: Mix a convenient quantity of the oil preferably in a wide test-tube with an equal volume of saturated solution of iodine in petroleum spirit, and allow the mixture to stand in direct sunlight. Under these conditions a peculiar insoluble spongy polymer of one of the fatty acids is formed.

Other Oils.—Other oils which are used in conjunction with pigments, in some cases only with artists' colours, are:

Poppy-Seed Oil.

Specific gravity ..	0.924-0.927
Saponification value	190-197
Iodine value ..	133-156 (Wijs)

Castor Oil.

Specific gravity ..	0.960-0.968
Saponification value	176-184
Iodine value ..	82-90 (Wijs)

Sunflower Oil.

Specific gravity	0.924-0.926
Saponification value	188-194
Iodine value	119-135 (Wijs)

Perilla Oil.

Specific gravity ..	0.932-934
Saponification value	189-190
Iodine value ..	203-206 (Wijs)

Oiticica Oil.

Specific gravity	0.9673-9679
Saponification value	186-190
Iodine value	139-152 (Wijs)

Safflower Oil.

Specific gravity ..	0.914-0.9285
Saponification value	177-197
Iodine value ..	116-122 (Wijs)

Soya-Bean Oil.

Specific gravity ..	0.924-0.927
Saponification value	190-194
Iodine value ..	121-136 (Wijs)

Rape-Seed Oil.

Specific gravity ..	0.911-0.917
Saponification value	170-178
Iodine value ..	93.5-106.5 (Wijs)

Menhaden Oil.

Specific gravity ..	0.929-0.933
Saponification value	190-195
Iodine value ..	150-170 (Wijs)

Whale Oil.

Specific gravity ..	0.917-0.927
Saponification value	188-192
Iodine value ..	110-128 (Wijs)

Sperm Oil.

Specific gravity ..	0.875-0.882
Saponification value	120-147
Iodine value ..	70-96 (Wijs)

Fish oils can sometimes be detected by the smell, when the suspected oil is rubbed on the palm of the hand. A good test devised by H. N. Copthorne is as follows: 100 drops of the oil are dissolved in 6 c.c. of a mixture containing equal parts of chloroform and glacial acetic acid. Bromine is added drop by drop until a brown coloration remains. After ten to fifteen minutes the test-tube containing the above is placed in a beaker containing boiling water. Linseed and other vegetable oils will clear up completely within a few seconds, while a fish oil will remain cloudy and precipitate an insoluble bromide at the bottom of the tube within a short time. It is quite easy to detect 10 per cent. of fish oil in vegetable oils by this method, and with a little practice even 5 per cent. of a fish oil is clearly recognisable.

In the case of boiled oils it is necessary to remove the metallic constituents before adding the bromine. This is preferably done by shaking with a 10 per cent. solution of nitric acid saturated with potassium nitrate. If both the oil and the acid are warmed up previous to shaking in a separating funnel, the separation will be almost immediate. Another test devised by Better and Szimkin (*Fettenhem Umschau*, 1934) also gives very good results, and is as follows: 3 c.c. of the oil are dissolved in 3 c.c. glacial acetic acid and 4 c.c. chloroform. If the mixture should not be clear, dilute it with a little more chloroform. Now add 20 drops of 10 per cent. bromine-chloroform mixture and 10 drops of Hanus iodine solution. Shake the mixture well, and in a short time it should become a deep green if fish oil is present. Should the green colour not appear after say five minutes, add a further 20 drops of bromine-chloroform mixture. Should the oil being tested contain only a small amount of fish oil, a further 10 drops of Hanus solution may be necessary, followed by a final 20 drops of bromine-chloroform mixture; after each addition the mixture must be well shaken. It is claimed that 5 to 10 per cent. of fish oil can then be detected. Should the oil be very dark in colour, then 0.75 gram of the sample should be taken. In every case, if there is fish oil present, the dark green coloration will be unmistakable.

Weight of Oils at 60° F.

						<i>Pounds per Gallon.</i>
Castor oil	9.62
Hemp-seed oil	9.27
Raw linseed oil	9.32
Boiled linseed oil	9.42
Menhaden oil	9.31
Poppy-seed oil	9.25
Sunflower oil	9.25
Safflower oil	9.14
China-wood oil	9.41
Perilla oil	9.33
Oiticica oil	9.67
Soya-bean oil	9.16
Turpentine	8.67
White spirit	8.00

The Hanus solution used above is prepared by dissolving 13.2 grams of iodine in 1,000 c.c. glacial acetic acid, then add

enough bromine to double the halogen content (about 3 c.c.). The iodine may be dissolved more quickly by gentle heat, but the solution must be cold before adding the bromine. Keep the solution in a dark brown or yellow bottle.

Turpentine and White Spirit.—American turpentine is chiefly obtained from the Georgia pine (*Pinus Australis*) and French turpentine from *Pinus maritima*, especially from the Departments of Landes and Gironde. Russian turpentine is obtained from the Scotch pine (*Pinus sylvestris*). There is also stump or American wood turpentine. American turpentine is a clear and water-white product, and weighs about 8 lbs. 10 ozs. to the gallon. The specific gravity ranges from 0.862 to 0.875 at 15.5° C. The boiling point is about 160° C., and it is completely distilled at 170° C. If adulterated, the usual products are rosin oil and products of petroleum.

If a small quantity of turpentine is evaporated in a small evaporating basin, there should be practically no residue left. Should rosin be present, there will remain a sticky deposit, giving off when ignited the odour of rosin. If a few drops of turpentine are placed on a sheet of white paper, all traces should have disappeared within half an hour if the spirit is pure, but if adulterated with rosin oil a distinct oily stain is left. Another useful but simple test is to place about 10 drops of the suspected turpentine on a watch glass, and float it in an evaporating basin containing water at 170° F. If the oil is pure, it will have evaporated away, leaving the glass quite dry in seven minutes; but if adulterated with a petroleum product, it will not have completely evaporated in that time. A further test to detect the presence of aldehydes or a poorly refined turpentine is known as the phloroglucinol test, and is carried out as follows: A special test solution is made up:

- 1 part of hydrochloric acid.
- 1 part of 5 per cent. phloroglucinol in ethyl alcohol.
- 1 part of glycerine.

To an equal part of turpentine add a similar quantity of the above reagent. If free from aldehydes, etc., the colour should be a pale pink or light yellow; a dark brown or red coloration indicates a turpentine of inferior quality.

The polymerisation test for turpentine as required by the B.S. specification is carried out as follows: 5 c.c. of the

turpentine is slowly added to 20 c.c. pure sulphuric acid contained in a Leffman-Beam bottle as used for milk testing and placed in a beaker of iced water. The bottle is shaken frequently and the temperature should not be allowed to rise above 60° C. When the mixture of turpentine and acid no longer gets warm after shaking, the bottle is well shaken and then placed in a beaker of water and heated to 60° to 65° C. for ten minutes, the bottle being taken out at intervals and well shaken. After this period the bottle is taken out and brought to room temperature and sulphuric acid added to bring the liquid up to the top mark in the narrow neck of the Leffman-Beam bottle, and should then be well centrifuged. If a Leffman-Beam apparatus is not available, a substitute can be made by using the back wheel of a bicycle, the bottle being enclosed in a wooden case, or the bottle may be allowed to stand over night, after which the volume of the unpolymerised residue can be read off.

On account of the high price of turpentine, large quantities of petroleum substitute known as *white spirit* or turpentine substitute are now used in the paint trade. The specific gravity is usually about 0.800 at 60° F. A good test for these substances is known as the copper strip test, and is performed as follows: A piece of polished sheet copper 2 inches by $\frac{3}{4}$ inch is placed in a porcelain dish. Now add 25 c.c. of the sample to be examined, and place the dish on a water bath or kitchen pan and evaporate off the volatile portion. If the sample contains any sulphur, the copper slip will be black or of a grey colour.

Another useful test consists in first preparing a sample of resinates thus: Take some W.W. rosin—say 100 parts—and melt it in an aluminium pan. Cook into the melted rosin 0.75 part by weight of litharge and 0.25 part by weight of manganese dioxide. Keep the temperature at 475° F.; when the oxides have properly reacted, which will be shown by the brightness of the solution, allow any undissolved material to

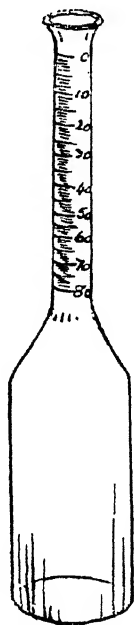


FIG. 6.—LEFFMAN - BEAM BOTTLE.

settle to the bottom of the pan, and pour off the clear resinate into a pan or tin to harden. When cool, it can be broken up into small pieces.

In order to make an oil bath, take another pan and have a tin support over the top of the pan consisting of a strip of metal containing two holes in which the two test-tubes can be

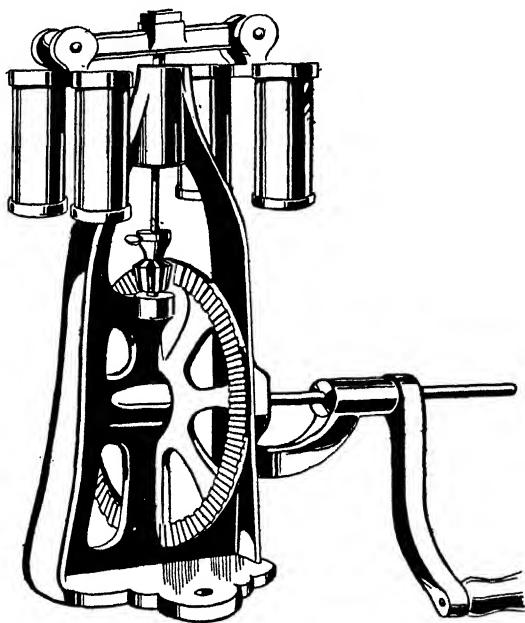


FIG. 7.—LEFFMAN-BEAM MACHINE.

placed, and having filled the pan a little over half full with linseed or rape oil, heat up to 425° F., and then insert the two test-tubes, each containing 5 grams of the varnish base. Now measure out 5 c.c. of genuine turpentine and 5 c.c. of turps substitute. When the temperature of the oil bath has reached 450° F., add the turpentine to one test-tube and the substitute to the other. Mix the resinate and thinners by stirring with

two glass rods with an up-and-down motion for about twenty seconds; then insert a small air condenser into each tube, consisting of a piece of glass tubing about 6 inches long fitted to a cork. Keep the tubes in the oil bath three minutes from the time the thinners are added, then remove both test-tubes and compare them for colour and clearness of product. They should be quite clear, a poor substitute invariably giving a cloudy result. During recent times the kauri-butanol test has been used when determining the solvent properties of various types of petroleum thinners. Take some finely powdered kauri gum (100 grams) and dissolve it in 500 grams of butyl alcohol at 240° F. and heat to the boiling point until the gum is entirely dissolved. Cool the flask and add butyl alcohol until the ratio is restored to 100 grams gum and 500 grams butyl alcohol. Allow the mixture to stand for four days (ninety-six hours) in a well-stoppered bottle, and after the specified time decant off the supernatant liquid into another clean bottle. Now take a flat-bottomed flask—a wide-mouthed boiled flask answers very well—put in 20 grams of the kauri alcohol mixture, and place on a white piece of paper having black printing on it. Place the turpentine substitute to be tested in a burette, and run it into the mixture in the flask, keeping the mixture at 77° F., and continue the addition until a point is reached where the printing becomes blurred or hazy. The number of c.c. that have been taken will denote its solvent properties. The flash point (Abel close test) should not be less than 78° F. If a distillation test is carried out in accordance with the B.S.I. requirements, if 100 c.c. of sample is taken, then not less than 80 c.c. should come over below 190° C. and not less than 90 c.c. below 200° C.

(2) Standard Solutions for Testing.

Dilute sulphuric acid	..	1 part by measure poured into 5 parts of distilled water.
Dilute hydrochloric acid		1 part in 3 of water by measure.
Dilute nitric acid	..	1 part in 3 of water by measure.
Dilute acetic acid	..	Equal parts of acid and water.
Sodium hydroxide	..	Dissolve 1 part of the caustic by weight in 20 parts of water.
Potassium hydroxide	..	Dissolve 1 part by weight in 20 parts of water.
Calcium hydrate (lime water)		Dissolve lime in water; allow to stand; then filter.

Ammonium carbonate ..	Dissolve 100 grams of the salt in 300 c.c. of distilled water; add 100 c.c. of 0.880 ammonia and make up with water to 500 c.c.
Ammonium chloride ..	Dissolve 100 grams of the salt in 400 c.c. water, and when dissolved make up to 500 c.c.
Ammonium oxalate ..	25 grams of the salt in 500 c.c. water.
Ammonium hydrate (dilute)	1 part by volume to 2 parts of water.
Ammonium sulphide ..	Purchased ready for use.
Potassium iodide ..	20 grams of the salt in 500 c.c. water.
Potassium ferricyanide ..	50 grams of the salt in 500 c.c. water.
Potassium ferrocyanide	Same quantities as above.
Barium chloride ..	25 grams of the salt in 500 c.c. water.
Lead acetate	50 grams of the salt in 500 c.c. water and 1 c.c. strong acetic acid.
Silver nitrate	20 grams of the salt in 500 c.c. water.
Cobalt nitrate	5 grams of the salt in 50 c.c. water.

(3) The Flame Test.

Take a platinum wire about 2 inches long. Cut off a piece of glass rod about 2 inches, and hold one end in the Bunsen flame to soften it. When soft, push one end of the wire into the glass rod; when cool, the wire will be fixed firmly in the rod.

Now heat the wire in the non-luminous part of the flame, and then clean it by dipping into a little hydrochloric acid. Again heat and dip the wire once more into the acid, and repeat the operation until hardly any yellow colour appears in the Bunsen flame when the wire is held in it. Now dip the wire into the substance to be tested, holding the wire in the upper part of the flame and noting the colour produced.

Coloured Flames.

				<i>Colour.</i>	<i>Shade.</i>
Calcium	Red	Yellowish to orange.
Barium	Green	Yellowish.
Strontium	Red	Crimson.
Sodium	Yellow	Intense.
Potassium	Violet	Pale (view through blue glass).
Zinc	Green	Bluish.

SECTION IV

SOME PHYSICAL TESTS

Specific Gravity.

THE specific gravity is the weight of a definite volume of substance, considered as a compact body, compared with water as unity. The determination is carried out by means of a specific gravity bottle, and the method of determination is applicable to both liquids and solids (dry powders). The bottle has a capacity of 50 c.c., with a thermometer ground in the central neck, and a stoppered capillary tube in the side neck (Fig. 8). The empty bottle is first carefully weighed. The stopper is now removed from the capillary tube, the thermometer taken out, a small glass funnel placed in the neck, and the bottle filled with distilled water. The thermometer is now replaced. This causes some excess of water to come out by the side capillary tube. Place the stopper on the capillary tube and carefully wipe and dry the bottle and weigh it. If the manipulation has been carefully carried out, the bottle may be found to contain about 49.982 grams of water at 15.5° C. or 60° F., or approximately 50 grams, the weight found being the bottle plus liquid (water) minus the empty bottle. This weight multiplied by 0.02 reduces the weight in grams to a specific gravity of 1, usually written 1.000. The *specific gravity* of any liquid is the weight of an equal volume of the liquid compared with water expressed as unity, and may be heavier or lighter than water.

In determining the *specific gravity* of a pigment, the weight of distilled water as previously explained having been ascertained, also the weight of the empty bottle, the pigment (about 10 grams) is introduced into the dry bottle, and the whole is weighed, the weight of the pigment being obtained by difference.



FIG. 8.—SPECIFIC GRAVITY BOTTLE.

The bottle is now filled with water in the same manner as before, and the bottle is well shaken to remove air bubbles, or gently heated, the stopper replaced, any excess water wiped off, and the bottle carefully dried and then weighed again. The ratio of the weight of the pigment to the weight of the liquid displaced by it is the specific gravity of the pigment. Sometimes turpentine or benzine is substituted as the liquid in the place of water.

In the case of *stiff pastes or liquid paint* a simple method can be used. This method is not strictly accurate, but for all practical works purposes is sufficiently correct. A standard cubic inch measure made of gun metal and having an exact counterpoise weight is employed. In the case of a paste, say zinc white, the measure is very carefully filled, and at each addition the paste is well pressed down with a small spatula, and when the measure is quite full, levelled off. In the case of a liquid paint, the measure is simply filled up, but prior to this the sample should be well stirred to get rid of air bubbles. This is also carefully levelled off. At least three different weighings are made in order to get a correct average of a cubic inch of the material. The weight in grams of a cubic inch of paste or paint minus the weight of the container multiplied by 0.6108 gives lbs. (avoirdupois) per gallon.

Weight in grams $\times 3.8058$ = lbs. per cubic foot.

Weight in grams $\times 0.06103$ = specific gravity.

The *apparent gravity* of a substance is the weight of a definite volume of substance in its natural state with included air, and like specific gravity is compared with water as unity. In the case of dry pigments, fill a brass container of exactly one cubic inch capacity and supplied with a counterpoise weight with the dry powdered pigment, tapping it gently on the sides. The tapping can best be performed by a glass rod with a rubber end. When quite full, level off with a spatula and weigh. The weight in grams divided by 16.387 will give the apparent gravity. At least five different determinations should be made in order to obtain the average weight. The apparent gravity of the same pigment will vary according to the method of filling the brass container, a loose filling giving a lower apparent gravity than when well pressed.

The following are the *average specific gravities of pigments* as determined by Dr. H. A. Gardner:

White lead (basic carbonate)	6.81	Burnt umber	3.80
Basic sulphate of lead ..	6.41	Brown oxide (50 per cent. Fe_2O_3)	3.35
Zinc oxide	5.66	Mineral brown (45 per cent. Fe_2O_3)	3.34
Zinc oxide leaded 35 per cent.	5.95	Chromium oxide	4.95
Lithopone	4.30	Litharge	9.40
Barytes	4.45	Orange lead	8.80
China clay	2.62	Red lead	8.80
Whiting	2.71	Chrome green	3.90-5.08
Venetian red (20 per cent. Fe_2O_3)	3.05	Green earth	2.75
Red oxide (40 per cent. Fe_2O_3)	3.45	Lime-proof green	2.80
Red oxide (95 per cent. Fe_2O_3)	4.95	Prussian blue	1.85
Indian red (90 per cent. Fe_2O_3)	4.92	Ultramarine	2.35
Ferric oxide (98 per cent. Fe_2O_3)	5.15	Chrome yellow	6.00
Ochre	2.80	Lamp black	1.78
Raw sienna	3.27	Carbon black	1.81
Burnt sienna	3.95	Drop black	2.64
Raw umber	2.65		

Settling Property.

The settling property of pigments depends to a great extent on the specific gravity, but differences in texture and particle size, and whether a pigment is crystalline or amorphous, play an important part. Substances like asbestine, having needle-shaped crystals, settle slowly, and will hold up heavier pigments which otherwise would sink rapidly. A pigment containing many aggregates and made up of coarse and fine particles always settles unevenly, the coarse particles settling rapidly, and the fine portion remaining in suspension for a much longer time. Apart from these various physical conditions, a settling test can furnish much useful information in the hands of an observant worker who is regularly carrying out the test.

The test is performed as follows: A tube closed at one end and having graduations up to 50 c.c. (each c.c. being divided into tenths), measuring 22 inches long and $\frac{1}{2}$ inch diameter, is fitted with a rubber stopper. This tube when in use can be conveniently clamped in a burette stand. Three grams of the pigment are weighed out and placed in a mortar, a small quantity of distilled water added, and the whole well rubbed

for three minutes. The pigment is then transferred to the tube by means of a small glass funnel. The mortar is carefully washed clean by means of a wash bottle and the liquid made up to 47 c.c. The rubber stopper is then replaced and the tube, having been taken in the hand at the stopper end, is turned perpendicularly up and then down exactly twenty times, once up and once down being counted as one. By this means the pigment is thoroughly mixed at the end of the twentieth up and down motion. The tube is fixed in the clamp of the burette stand, and the pigment allowed to settle for exactly fifteen minutes, when the level arrived at is read off and recorded.

Taking a pigment like zinc oxide as an example, the following results have been obtained:

					<i>From 47 c.c.</i>
(1) Very fine particle size German activated	31 c.c.
(2) Fine cosmetic French oxide	29 "
(3) British Pharmaceutical oxide	28 "
(4) White Seal oxide	20.4 "
(5) Red Seal oxide	19.2 "
(6) French Process American	18.5 "
(7) Coarse American	12 "

Though no great reliance can be placed on this test as a guide to particle size, when carefully carried out on a fumed pigment like zinc oxide, a rough indication can be obtained as to what to expect as regards the fineness of particles. In all settling tests the liquid medium used causes considerable variation in the rate of settling. For instance, most pigments are found to settle quicker in aviation petrol than in water, benzine or turpentine. In all settling tests the time should be taken with a reliable stop-watch. In the case of all pigments the "time of settling" is much influenced by the amount of moisture the pigment contains, a bone black containing, say, 7 per cent. of moisture settling slower than one that is moisture free.

Oil Absorption.

The B.S. method is as follows: Ten grams of the pigment are placed on a white porcelain, ground glass or marble slab, and raw linseed oil is gradually added and rubbed in thoroughly with a palette knife until a stiff paste of smooth consistency is obtained. The weight of oil used, multiplied by 10 (*i.e.*, cal-

culated as a percentage of the dry pigment), shall be taken as the oil absorption of the pigment.

Another way of determining the oil absorption employed in some paint works is to weigh out 20 grams of the pigment and place it in an 8-oz. beaker. Then having filled a burette with refined linseed oil, run in a little at a time, so that sufficient liquid is added to just moisten the dry powder. Stir with a glass rod having a flat end, and continue adding the oil till a stiff paste is formed. The number of c.cs. of oil used, multiplied by 5, will give the percentage of oil to be mixed with 100 grams of pigment.

Another method now much used by colour and paint houses is that devised by Dr. H. A. Gardner. The test is as follows: When mixing a liquid and a pigment, a point is arrived at when, independent of the mechanical forces employed in actual grinding, the surface of each pigment particle is thoroughly wet by the liquid, and the pigment mass becomes completely saturated. This point represents the oil absorption property of the pigment, and is expressed by a factor which is termed the oil absorption factor. This factor is therefore a measure of the quantity of an oil or liquid that is required thoroughly to wet the particle surface of the pigment mass. The factor is found by estimating the number of c.cs. of a refined linseed oil to saturate 20 grams of pigment. It is then stated as the amount of oil required for 100 grams of pigment.

In designing a paint, the oil absorption factor is most valuable for determining the amount of oil necessary to grind each pigment to paste form, and to produce a certain desired consistency. The amount of oil necessary for pigment saturation is directly proportional to the specific surface of the pigment mass existing at the point of saturation. The specific surface of the mass is relative to its degree of particle subdivision or fineness; it is also a measure to a large extent of the fineness of the pigment. The practical advantage of knowing the oil absorption factor lies in the information it gives concerning the following physical conditions of the pigment:

- (I.) Relative amount of surface in the pigment mass.
- (II.) State of subdivision of pigment particles.
- (III.) Comparative specific surface of different pigments.
- (IV.) Variation in fineness of various lots of the same substance or pigment.

Dr. Gardner gives the following table:

Oil Absorption Factors on Some Pigments.

<i>Pigment.</i>	<i>Low Oil Absorption Type.</i>	<i>High Oil Absorption Type.</i>	<i>Average Type.</i>
Basic carbonate white lead ..	15	22.5	30
Basic sulphate white lead ..	26	32	30
Zinc oxide	47.6	54.1	52
35 per cent. leaded zinc ..	31.3	36.5	32
Lithopone	22.75	38.5	33
Asbestine	32	50	50
Barytes	13	15	13.5
Blanc fixe	23	36	30
China clay	41.5	53	51
Gypsum	26	35	33.5
Silica (crystalline)	20	28	23
Silica (amorphous)	30	38	32
Talc	40	65	60
Whiting	28	35	32

The test is carried out as follows: The apparatus consists of a small wide-mouthed bottle with rubber cork, a 50 c.c. burette, a porcelain dish 5 inches diameter, and a 4-inch nickel spatula with a blunt end. The sample to be tested should be first placed in the small wide-mouthed bottle and well shaken so as to ensure elimination of any packed particles or lumps; 20 grams are then weighed out carefully and placed in the dish. The refined linseed oil is then run in from the burette drop by drop, the rate being one drop per second. As the absorption of the oil increases, the rate of flow is decreased. The oil should drop in the centre of the pigment, and the dry pigment that has not been wetted should be lifted up by the spatula from the outer edge and placed over the oil, so as to bring all the oil surface in contact with the pigment. As the pigment particles become wet with the oil, they tend to coalesce and form small lumps of paste. These lumps should be kept distributed throughout the mass. As the absorption progresses, the small lumps form larger lumps, and finally one large lump. The "end point" is very near the formation of the large lump, and at this stage the oil must be added very slowly and carefully. When a smooth ball has formed, the end point is reached.

Example: 20 grams of zinc oxide; oil used, 10.2 c.c.; $10.2 \times 5 = 51$.

All these methods can only be looked upon as a guide; they are of comparatively no use in works practice. The oil absorption of a pigment is in the opinion of the writer much better carried out, provided sufficient sample is available, by using a model laboratory single roller pan mill and treating 500 grams of pigment, carefully adding a weighed quantity of oil, and weighing back the remainder. By this means the nearest approach, as far as the adaptation of laboratory tests to works practice is concerned, can be obtained. The oil absorption of a pigment, as shown on amalgamating and mixing with refined linseed oil by mechanical means, differs from the figures obtained by rubbing out with a palette knife, and, moreover, will differ with the type of mechanical mixer employed. In large works where big quantities of zinc oxide paste are made, it is usual to use a plant similar to a "Torrance Combination" consisting of one, and in some cases two, roller mills in tandem, with a large positive single roller pan mill above. Such pan mills are usually 8 feet in diameter with a roll 5,000 lbs. in weight, having a well-adjusted scraper and gate discharge, which deliver the ground and mixed paste on to the triple roller mill, which must be carefully adjusted to give the paste a good finish and appearance, no matter how stiffly the material may be mixed.

The advantage of making zinc oxide paste by this method will be seen when it is considered that the chaser roll exercises a condensing action on the pigment, thus requiring a lesser percentage of oil to form a paste than would be necessary in an ordinary horizontal or pug mixer. As a matter of fact, it is well known in paint practice that if 300 lbs. of dry zinc oxide are emptied into the chaser, and the crushing roll run over the pigment for, say, thirty minutes, and the zinc oxide is then returned to the original package, the container will be a little more than half full. In other words, the zinc oxide has been condensed to a little more than half its original bulk. In practice the dry zinc oxide is placed in the chaser with sufficient oil to lubricate the material while being mixed, and the weight of the crushing roll gives enough of the condensing action to make it possible to get along with a smaller percentage of oil than is required when amalgamating in a horizontal mixer or vertical pug mill. It is on this account that the use of a single chaser pan mill for laboratory use is advocated, as the oil

absorption figure obtained is nearer the truth, and more in accordance with works practice than any other method.

On further considering oil absorption or the wetting of pigments, it must not be forgotten that in mixing a pigment with a liquid a point is reached when, independent of mechanical force, the surface of each particle is thoroughly wet by the liquid and the pigment mass becomes entirely saturated.

Dr. Gardner defines oil absorption as "the measure of the quantity of a given oil or liquid required thoroughly to wet all the absolute particle surface of a pigment mass." The amount of oil required for pigment saturation or wetting is directly proportional to the specific surface of the pigment mass existing at the point of saturation. The specific surface of any mass such as zinc oxide, lithopone, barytes, chalk, etc., is relative to the degree of particle size or fineness. It has been shown by Brown (U.S.A.) that small particles form aggregates, and that the electrical charges of the particles themselves cause a coalescence. Other factors apart from particle size which play a part are:

- (a) Viscosity of the vehicle.
- (b) Pigment vehicle ratio.
- (c) Force of flocculation.

Flocculation is a condition of aggregation, and is that condition or state when the dispersed phase ceases to be dispersed uniformly, and exists in groups or clusters, the individual units (particles) of which are closely held together, apparently by the residual surface tension existing in the interface between dispersed and continuous phases. When we use the term "flocculation" we imply three things:

- (I.) A previous state having existed in which the discontinuous phase was dispersed in a continuous phase. For instance, to describe any mass of particles—a soil, for instance—we should say that it was "minutely discontinuous."
- (II.) The units (particles) of the discontinuous phase, when brought into contact with each other owing to currents or mechanically produced motion, form groups or flocculates.
- (III.) Adhesion which may be due to surface tension of the touching units.

Now if we take a pigment like zinc oxide, and use no mechanical force whatever, we have an undispersed clump of pigment particles immersed in a liquid vehicle, say linseed oil.

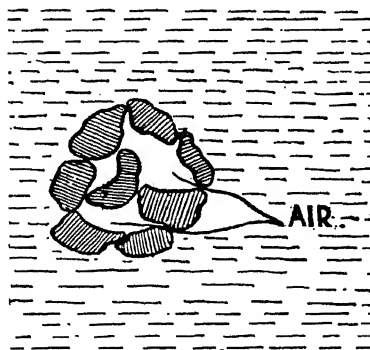


FIG. 9.—UNDISPERSED CLUMP OF PIGMENT PARTICLES IMMERSED IN A LIQUID MEDIUM. THE INTERIOR SPACES ARE OCCUPIED BY AIR.

Fig. 9 shows a rough sketch as it would appear under magnification. The vehicle is in contact only with the exterior of the

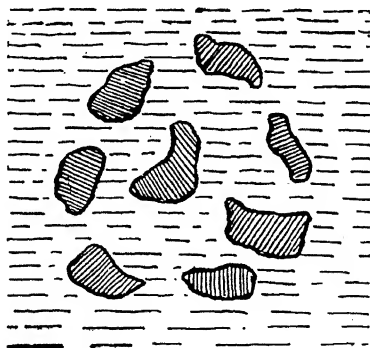


FIG. 10.—PARTICLES DISPERSED AFTER BREAKING UP THE CLUMP.

clumps; the interior contains air spaces, and the finer the particles and the greater the number of air spaces, so will the oil absorption be higher.

Now if by mechanical means (palette knife) the clumps are broken up, they will become completely dispersed as in Fig. 10.

The air spaces have become eliminated, and the vehicle is presumably in complete contact with each particle. Specific gravity is stated to have no effect on these phases, but surface energy in the pigment vehicle has, and if the particles, by more mechanical rubbing, are brought into contact with each other, they will loosely adhere (presumably owing to surface energy), forming a flocculate, and the intervening spaces between the pigment particles will now be seen to be filled with the vehicle (oil) and the mass will be a stiff paste (Fig. 11).

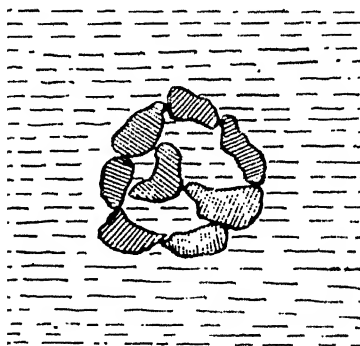


FIG. 11.—PARTICLES LOOSELY ADHERING TO FORM A FLOCCULATE, THE SPACES BEING FILLED WITH THE LIQUID MEDIUM.

If more oil is added, then the paste loses its yield value, and becomes soft; in fact, it may become fluid, and no longer bears the slightest resemblance to its former consistency. The reason for this is that a flocculated pigment is a structure which holds the mass together, giving it a plastic nature, but when the structure is destroyed, plasticity tends to vanish. A very simple experiment will illustrate this.

Make up a stiff paste with zinc oxide and paraffin oil (kerosene). It will be noticed in the process of mixing the pigment and vehicle that an abnormal quantity of the liquid can be added without producing a mixture with a tendency to flow out under its own weight. This paste is decidedly plastic, and

possesses a yield value. When the consistency is correct, the mass will be sufficiently plastic to retain its form. If, however, a few drops of blown linseed oil are added and well rubbed in with a spatula, the effect is striking. The paste loses its yield value, and becomes very soft, and no longer has the slightest resemblance to its former firm consistency. In other words, the plasticity has gone, and the point of true oil absorption passed.

Let us now consider another aspect as regards the wetting of pigments, as this subject is of great interest to the paint manufacturer. The time of wetting depends upon wetting forces, viscosity of vehicle, the amount of mechanical work done upon the mixture, the particle size, and the forces of wetting between pigment and vehicle have a decided influence on true consistency.

By *wetting force* is meant the spontaneous force with which a liquid tends to spread upon and wet a solid, when the liquid is brought into contact with the solid, no external work of any kind being supplied.

In 1929 Dr. Bartell read a paper before the Paint and Varnish Section of the Seventy-eighth Meeting of the American Chemical Society at Minneapolis, in which he showed that the wetting of a powder could be quantitatively measured as regards the wetting or adhesion tension of a liquid towards a powdered solid. Dr. Bartell stated that good wetting was characterised by high adhesion tension and a low angle of contact between solid and liquid.

In order to demonstrate this, a modified Bingham and Murrey vacuum plastometer was used. The Bartell method of studying wetting involves measuring the pressure developed when a liquid displaces a gas (air) or another liquid from a compressed cake of powdered solid. Now Bartell has shown that the pores of a compressed powdered solid may be considered as a bundle of small capillary tubes, and the finer the particle size of the material, the greater number of tubes there are. Let us assume we have six blocks of a pigment $1\frac{1}{2}$ inches long and $\frac{1}{2}$ inch diameter, all of different grades. Let these be compressed with an equal force so great that they represent abnormally tight packing, say 52.7 lbs. per cubic foot.

Prepare four sets of six. Allow one set just to touch paraffin oil, the next refined linseed oil, the third lightly blown oil, and

the last set thick stand oil, no mechanical force being exerted. The rise of the liquid will then be due to four factors:

- (1) Number of capillary tubes (particle size).
- (2) Viscosity.
- (3) Surface tension.
- (4) Power to overcome occluded gas (air) expressed thus:

$$y = \frac{R H V G}{2 \cos \theta}.$$

Where y = surface tension.

R = radius of capillary tube.

H = height of liquid in tube.

V = viscosity.

G = gaseous pressure.

θ = contact angle between solid and liquid.

On observing the blocks, it will be seen that the more viscous the liquid, the slower the rise will be. Now take a second set of blocks. Crush them down, and apply gentle pressure as regards rubbing in oil, the amount of oil being noted. Take a third set, crush them down, and apply as much pressure as possible with a palette knife when rubbing up. Less oil will be taken in all cases than in the case of the samples lightly treated, to the extent of 1.5 to 2 c.c., thus confirming the statement previously made regarding the light and gentle action of the horizontal mixer as against the Torrance combination plant.

In concluding these remarks on oil absorption it may be stated that:

- (I.) Linseed oil should always be used.
- (II.) The acid value of the oil should be from 1 to 3, because the amount of oil used increases with the acid number, this difference being due either to a greater particle dispersion or to thickening caused by the formation of metallic soaps.
- (III.) If the oil absorption is made with other oils, then the results will be relative to the dispersing effect of the liquid used and the viscosity.
- (IV.) The moisture content of the pigment between small limits seems to have no effect as regards oil absorption.

Opacity of White Pigments.

The opacity of a white base can be determined as follows: Weigh out accurately 3 grams, say, of zinc oxide, and 0.3 gram of a standard ultramarine. Transfer both to a clean ground-glass plate, mix well, and add 1 c.c. of refined linseed oil from a burette, and by means of a palette knife work up the mixture to a nice smooth paste. Then give the paste a good mulling for three minutes, allow to rest for one minute, having previously collected the paste together carefully into a small heap. Then mull a second time for three minutes. Spread out the paste on a colourless glass slip (1×3 inches) having ground edges, such as is used for microscopical work. Having prepared the sample, take the standard and prepare a second sample of paste in the same way. Now bring the two glass slips together, and observe the appearance on the reverse side of the glasses. If both appear the same, then the opacities of the standard zinc oxide and the sample are equal. If the sample is weaker or stronger than the standard, then the ultra blue must be increased by 0.0273 or decreased by the same amount, by making up fresh lots of paste to compare with the standard, until the standard and sample match one another, and from these the opacity of a zinc oxide can be calculated.

Matching Colours.

The best way of matching dry colours is to place a small amount of each standard and sample on a piece of white paper and observe the colour and brightness. If we take two ultramarines, place 1 gram of each on a piece of white paper, so that the two samples are side by side and just touch one another; then fold the paper over and press down with a palette knife, which will have the effect of flattening out the two powders. Now carefully raise the paper and straighten out; it will be found that the standard and sample are side by side quite flat and smooth with the two edges meeting in the middle, when any difference in colour and brightness can be easily noted.

Colours that are ground in oil are always matched on glass. Dry colours can also be compared in this way, provided the same amount of oil is used each time when making up the paste. The two pastes are spread side by side, and just touching on a slip of colourless glass. To compare the colours the glass

slip should be turned over, and the colours viewed on the reverse side in a north light, when any difference in colour and tone can be detected at once.

Strength or Tinting Power.

The method consists in mixing a weighed amount of the sample pigment with a given weight of zinc oxide, and comparing the tint with a standard of known purity. The strength of a coloured pigment will depend on texture (fineness) and chemical composition. It is first necessary to make a paste of the colour to be tested, and then of the standard colour; using the same amount of pale refined linseed oil in each case, and rubbing up on a smooth clean glass slab, giving each exactly the same amount of rubbing. A white paste is also made consisting of White Seal standard zinc oxide also in pale refined linseed oil. One hundred milligrams (0.100 gram) of each coloured paste is then taken, and to these are added 2 grams of the white zinc oxide paste respectively. These are well rubbed up, and represent a 20 to 1 reduction in each case. The respective pastes are then placed side by side on a clear glass slip and compared. If the tinting strength of the standard be 100, the amount of standard paste must be varied until the colours match, usually the variation made being 5 per cent. (for example, 0.095 or 0.105). The amount of standard pigment being taken as 0.1 gram = A, then the amount required to match a given strength = B.

$$\frac{A}{B} \times 100 = \text{tinting strength.}$$

Grit Tests.

In examining pigments for grit three methods can be used. The first method consists in taking a weighed quantity of the pigment, say 25 grams, and having placed this in a beaker of 500 c.c. capacity, add white spirit or methylated spirit and stir well. Now wash through a previously dried 300-mesh standard sieve, assisting the passage of the finer particles by rubbing with a camel's-hair brush. The screen is then carefully dried, the residue transferred to a watch glass and weighed, and the amount found multiplied by 4 will give the percentage of grit or coarse particles, if 25 grams have been taken.

Another method which is much used is the Gallie-Porritt apparatus (Fig. 11). The distinctive feature of this method consists in suspending the powder under test in water, and supplying by a jet of water under pressure the mechanical force necessary to secure the passage of the fine particles through the sieve and the breaking down of any lumps. The apparatus consists of a metal funnel terminating at the foot in a short cylindrical outlet in which is inserted a shallow removable cup, on the bottom of which a wire gauze is mounted. The aperture is 25 mm. diameter, and the gauze may be of any desired mesh. The water under pressure is supplied by a tube fitted with a nozzle designed to discharge a spreading jet through the sieve, and the tube is so arranged that the discharge of the orifice in relation to the sieve can be adjusted. The tube is provided with a filter to ensure the removal of any solid particles from the water. This filter must be made from a gauze at least as fine as that used for the separation of the grit from the material under test, and must be of an area large enough to ensure a low velocity of flow to prevent undue loss of pressure. A similar arrangement is required in another tube, used to supply a gentle stream of water for wetting the powder and keeping the volume of the liquid in the funnel constant during the progress of the test.

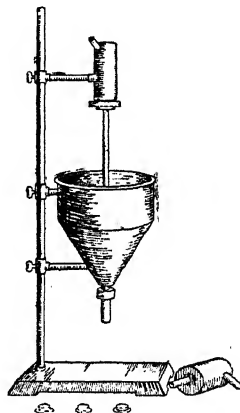


FIG. 12.—THE GALLIE-PORRITT GRIT-TESTING APPARATUS.

In using the apparatus, a quantity of the material to be tested is weighed out and transferred to the funnel, in which it is thoroughly wetted by a stream of water from the secondary supply, the treatment being continued until the funnel is about half filled with liquid. The high-pressure jet is then slowly turned on full, and the position of the nozzle under the liquid adjusted in relation to the sieve, until there is little or no disturbance on the surface of the liquid, and the level is, if anything, sinking. The secondary supply is now brought into use to maintain the level constant, and to wash down any solid matter

which may be adhering to the sides. When the most perfect operating conditions have been so attained, the discharge pipe below the sieve is completely filled with water, and it has been found that increasing the length of this column of liquid by adding a length of rubber pipe will tend to improve the efficiency of the apparatus. Samples of the discharge water can be taken from time to time during the progress of the test, and when it is obvious that the discharge is free from suspended matter, the rate of flow of the jet is reduced, any residual material adhering to the sides of the funnel washed down into the lower portion of the apparatus, and the jet then adjusted to the rate which just keeps the cylindrical portion full of violently agitated water. When the residual matter has been thoroughly washed in this way for a definite period, the jet is turned off, and the grit washed down into the cup. The milled union nut is then slackened off, and the discharge pipe and cup removed, and the contents of the latter washed with distilled water, drained, and transferred to an oven at 100°-110° C. to dry, and then weighed.

The following examples may be of interest:

					300 Mesh (Per Cent.).
Basic carbonate white lead	0.017
White Seal zinc oxide	0.019
35 per cent. leaded zinc oxide	0.150
Titanium oxide	0.020
Zinc sulphide	0.049
Antimony white	0.132
Best barytes	0.240
China clay	0.500

Another method very useful in detecting gritty particles is to make use of a gramophone record. One record may be used for several tests, and the records kept in a cabinet for comparison as standards for further batches of pigment of the same material as received. A gram of the pigment is placed on the record and carefully rubbed with the finger into the grooves, when differences in texture will at once be perceived. Some substances will feel coarse and gritty; others will feel soft and smooth. The samples can then be examined under a microscope, if desired, using a 32 mm. objective and a 12.5X eye-piece; by this means greater depth of focus is obtained.

Large crystals settle between the grooves of the record, and are found arranged with their facets parallel to the face of the disc, while, with a fumed pigment like zinc oxide, fine particles

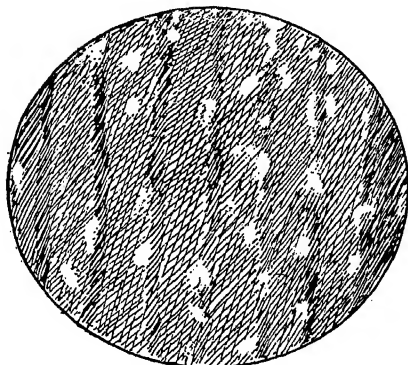


FIG. 13.—THE GRAMOPHONE RECORD TEST FOR GRITTY PARTICLES, SHOWING THE EFFECT PRODUCED BY A VERY COARSE PIGMENT.



FIG. 14.—THE EFFECT PRODUCED ON A GRAMOPHONE RECORD BY PARTICLES OF A FINE PIGMENT.

as well as aggregations can be easily shown. The accompanying illustrations, Figs. 12 and 13, clearly show the differences between coarse and fine samples.

Pigments Practically Permanent to Light.

- (I.) All the white pigments.
- (II.) *Yellow*.—Yellow ochres and in a less degree cadmium yellow, Naples yellow, and zinc yellow.
- (III.) *Reds*.—Madder red, Venetian red, red oxides, purple oxide, Indian red, and in a less degree red chrome, red lead, and para red.
- (IV.) *Green*.—Green oxides of chromium, ultramarine green, zinc green, and in a less degree chrome greens.
- (V.) *Browns*.—All the brown earths, raw sienna, and umber.
- (VI.) *Blues*.—Cobalt and ultramarine blues.
- (VII.) *Black*.—The blacks have all good permanency.

Lime-Proof Test.

The dry pigment (about 2 grams) is placed in a wide-mouthed screw-top bottle with 100 c.c. of saccharated lime water and well shaken, and then set aside to settle for twenty-four hours. The pigment is then filtered off and dried, and compared after rubbing up with refined linseed oil with the original untreated material.

The saccharated lime water is made as follows: Triturate 28 grams of slaked lime and 56 grams of white sugar in a mortar along with 600 c.c. of distilled water. After being well rubbed up, place in a 1,000 c.c. cylinder and allow to stand until clear, and then filter. The clear liquid is then used for the above test.

Pigments which are practically lime-proof are:

- (I.) *White Pigments* such as zinc oxide, lithopone, titanium oxide, blanc fixe, barytes, china clay, whiting and silica.
- (II.) *Yellow Pigments* such as yellow ochre, Naples yellow (antimony and lead oxides) and Indian yellow.
- (III.) *Red Pigments*.—Iron oxides, madder red, and in a less degree red lead.
- (IV.) *Brown Pigments*.—Any brown earth colour.
- (V.) *Green Pigments*.—Green earth, green oxide of chromium.
- (VI.) *Blue Pigments*.—Cobalt blue, ultramarine.
- (VII.) *Black Pigments*.—Any type of black.

Acid-Proof Test.

Under ordinary circumstances "the acid-proof test" should be made with a centinormal solution of the common acids, but for quick results a 5 per cent. solution of hydrochloric acid may be used, and any pigment not dissolving or changing colour can be said to be acid proof. To carry out the test, place 1 gram of the dry pigment in 15 c.c. of the dilute acid and stir with a

glass rod. Whiting will slowly dissolve with effervescence; on the other hand, Prussian blue will simply show a deeper colour.

Alkali-Proof Test.

This test is useful owing to the use of casein, silicate of soda, and other alkali binders; also on account of the caustic lime present in new walls, etc. To carry out the test, boil 1 gram of the pigment for five minutes in a large test-tube with 25 c.c. of a soda solution made by dissolving 40 grams of sodium hydrate in 1,000 c.c. of distilled water. Any pigment standing this test may be taken to be practically alkali proof.

- (I.) *White Pigments*.—Barytes, blanc fixe, asbestine, and to a less degree terra alba, whiting.
- (II.) *Red Pigments*.—Venetian red, Indian red, red and purple oxides, and in a less degree chrome red.
- (III.) *Yellow Pigments*.—Barium chromate, yellow ochres.
- (IV.) *Green Pigments*.—Green oxide of chromium, cobalt green, green ultramarine.
- (V.) *Brown Pigments*.—Raw and burnt sienna, iron and manganese browns.
- (VI.) *Blue Pigments*.—All classes of blacks.

SECTION V

SYNTHETIC RESINS.

AT the present time the paint and varnish trades have a wide range of synthetic resins to choose from—viz., straight phenol-formaldehyde resins, of which the bakelites soluble in drying oils and aromatic hydrocarbons may be taken as an example.

Secondly, modified phenol-formaldehyde resins soluble in drying oils, aromatic hydrocarbons, and also used in nitro-cellulose enamels, as well as paint and enamel vehicles, and a further modified class in which natural resins are introduced in the course of manufacture. Another class of straight phenolic resins are Durez, a non-skinning type, suitable for oil varnishes and mediums, both for interior and exterior use.

In the class known as Epok we have one of our oldest British types, a phenol-formaldehyde class modified with china-wood oil, which have given excellent results in oil varnishes, gloss paints, enamels, and stoving lacquers. The pure phenolic series of the Bekacite class offer the paint and enamel manufacturer an extensive range of products suitable for the formulation of all types of mediums, and are found as oil reactive and also non-reactive. The reactive types foam during the process of cooking, while the non-reactive do not. Another British class of synthetics are the Erinite resins—100 per cent. phenolic. Erinite 11 has a low acid value, and the varnishes made therefrom are extremely resistant to after-yellowing and are very suitable where pale shades are called for; moreover, basic pigments can be used without fear of excessive feeding-up taking place.

Another very extensive class are the Rezyl synthetics, of which we have saturated rezyls, unsaturated rezyls and glyptol modified with natural resins and known as Teglacons: the glyptol resins are formed by the condensation of polybasic acids and polyhydric alcohols—for example, by the condensation of glycerine and phthalic anhydride. Excellent varnishes can

be prepared in many cases having very low acid values, either by simple churning or the "cold-cut" method or by cooking in the usual manner. Various resins of this alkyd series are also known as Paranols and Paralacs.

Another series of British resins are the Albertols, of which there are oil-soluble and spirit-soluble types, and originated from research carried out by K. Albert and L. Behrend.

The oil-soluble albertols are very suitable for the manufacture of high-grade varnishes and enamels, especially where hardness of coat, resistance to moisture and durability on exposure are looked for.

Finally, we have the Coumarones, also known as rubber resins which are a class by themselves, being formed by the polymerisation of certain constituents of coal-tar naphtha. These resins vary from soft sticky varieties of dark colour to hard and pale types. They are soluble in drying oils and all ordinary thinners, and are of low acid value, but they have a tendency to yellow in conjunction with delicate shades.

Today, with the rapid increase of synthetic resins and the number of new types continually being brought forward, the identification of these products is becoming one of the most important branches of paint chemistry. Though a great deal has been written on this subject, there have been very few references relating to the identification of the various synthetics now available. The analysis of synthetic resins is difficult, due to the fact that the chemical reactions available relate to only a small number of those now being offered to the paint manufacturers, so that those examining paints and varnishes have had to rely on such tests as smell, melting point, viscosity and so on. Again, when examining a gloss paint or lacquer the resin is dissolved in a medium, and in the case of a lacquer a plasticiser is present, along with other solvents, so that many colour reactions are considerably changed, or are indefinite in character.

For the average paint-works chemist the test applied should be fairly simple and rapid, as in most cases the amount of material, especially recovered material, is usually small, so that complicated tests are out of the question. The following simple tests may be frequently found useful. As an example let us assume we have a "cold cut" varnish containing coumarone resin made by churning 8 lbs. of the resin in 1 gallon

of white spirit. First take 25 c.c. of the varnish or other convenient quantity, and distil off the spirit in order to recover the resin—that is, provided a sample of between 50 to 100 c.c. has been supplied. The difficulty of identification of the resin is then much reduced, and can be carried out by the Storch-Morawsky test, when an orange to brown coloration should result, or by a colour reaction with bromine. The Storch-Morawsky test is carried out as follows:

Take 2 grams of the resin, place in a small flask and add 10 c.c. of acetic anhydride, and heat over a small flame until a clear solution is formed, then cool. If the solution is cloudy, then it should be filtered. Before filtering moisten the filter paper with acetic anhydride. Place a small portion of the clear filtrate in a porcelain dish and add a drop of sulphuric acid. The following are the colour reactions of some of the synthetic resin types at present available:

Resin and ester gums : Purple changing rapidly to brown.

Straight 100 per cent. phenolics : No change.

Modified phenolic resins : Wine red changing to dark brown.

Resin modified maleic acid resins : Wine red changing to olive brown.

Urea-formaldehyde resins : No change.

Alkyd resins : Light greenish-brown.

Aldehyde resins : Deep brown changing to yellow on further addition of acetic anhydride.

Coumarone resins : Orange to brownish-red.

If the resin is not available the tests can be tried with the varnish, but in this case the colour changes are more difficult to tell with the oil present, as it somewhat masks the results. The author has found the best way in such cases is to have a set of standard varnishes of known composition of the different resins, about twenty-four in all, and when carrying out the test compare results as regards colour change.

Another test for coumarone resin is a colour reaction with bromine described by Dr. H. A. Gardner. Coumarones give a permanent red colour with bromine in the presence of glacial acetic acid. Take 1 c.c. of a 10 per cent. solution of the resin in chloroform and further dilute it with 6 c.c. chloroform and 1 c.c. glacial acetic acid. Now shake up well and add 1 c.c. of a 10 per cent. solution of bromine in chloroform, shake up again, and then allow to stand. If coumarone resin is present, a

permanent red colour will develop. It should also be remembered that coumarone resins are unsaponifiable, and when refluxed with N/1 caustic alkali no saponification figure should be obtained, and there is practically no acid value. Again, on melting this resin the vapours evolved smell strongly of coal-tar oils. When an oil-varnish sample is under examination, the unsaponifiable portion of the whole is first isolated. This is then dissolved in a little ether, transferred to a test-tube and evaporated to dryness. Then a plug of glass wool is placed in the mouth of the test-tube, and the tube heated until the mass fumes strongly and condense in the glass wool. The wool is then transferred to a clean dry test-tube and covered with acetic anhydride, allowed to stand a minute or two, and then poured off and two drops of H_2SO_4 , specific gravity 1.53, added. In the case of coumarone resins a deep orange colour should develop.

Aldehyde Resins.

These resins are also unsaponifiable, and are chiefly used in nitro-cellulose lacquers. The best way of dealing with such mixtures is to follow Spitz and Hoenig's method. First isolate the resinous matter in the presence of the nitro-cellulose by placing the lacquer in a separating funnel, and precipitating nitro-cotton by excess of benzene. The benzene solution will contain the resin; distil this off to low bulk and then submit it to destructive distillation. The presence of aldehyde can then be detected by the smell, which resembles strong acetic acid, and then further confirm by the colour test previously given.

Urea-Formaldehyde Resins.

These are very hard and tough resins.

Take a few grams of the resin or, say, 10 c.c. of the varnish and free the latter from the solvent (the thinners) by heating, then reflux with ten times as much N/1 alcoholic KOH, connecting the reflux condenser by means of a glass tube, having the end of the tube immersed in a beaker of distilled water. Ammonia due to the decomposition of the urea will be given off, and can be identified by the smell and by dipping red litmus paper in the water. Now take the beaker of water after refluxing about half an hour and neutralise with N/10 HCl and evaporate

to dryness on the water bath. The residue can then be identified as ammonium chloride. The microscope is very useful in this case, as the crystalline structure of the residue can be compared with a residue prepared from the pure salt.

According to Metz (*Kunststoffe*, 1937, No. 10, 269) formaldehyde is liberated when urea-formaldehyde resins are heated with H_2SO_4 (20 per cent. solution) and the aldehyde distilled off by steam. The resin can then be identified by testing either with ammonia-silver solution, warming the mixture in a test-tube on the water bath, when a mirror of metallic silver will form if aldehyde is present, or by oxidation with iodine in KOH solution. The ammonia-silver is made by mixing 10 c.c. of a 5 per cent. solution of silver nitrate with 5 c.c. of a 10 per cent. solution of ammonia.

Phenolic Resins.

In the absence of rosin the Storch-Morawsky test previously described is negative, while it is positive if rosin is present, the wine-red colour quickly passing to an olive brown. Taking a varnish suspected of containing this type of resin, the solvent thinners are first evaporated off, and the remainder fused with caustic potash in a large silica crucible. The mass when melted is heated for five minutes, and then dissolved out with hot water and acidified with H_2SO_4 . The phenol which is then freed is distilled over with steam. The distillate is then made alkaline with NaOH, cooled and coupled with diazotised *p*-nitraniline. In the presence of phenol a red precipitate is formed.

Another test using fast red 3 G.L., a stable diazo-compound of 2-nitro-4-chloraniline, has been developed by Kappelmeier (*Farben Ztg.*, 1937, 42, 561) and is very good and reliable. Take 5 grams of the varnish, free it from volatile thinners, and mix with 20 c.c. N/1 alcoholic KOH solution. Evaporate to dryness on the water bath. Take up with 10 c.c. N/1 alcoholic potash, cool, filter and treat with 5 c.c. of the special reagent—that is, 0.5 gram fast red G.L. in 5 c.c. distilled water and 1 c.c. N/4 HCl. In the presence of phenol a dark red precipitate is obtained.

Alkyd Resins.

Under this heading a number of resins are offered to the trade under the names of Rezyls, Glyptols, and Paralacs.

One of the best and most reliable methods is the isolation of the phthalic acid and then to examine the sublimed crystals under the microscope.

Take a test tube, place it in 3 c.c. of the varnish to be tested, and heat over a small flame until the solvent has been driven off. Now raise the temperature, and having connected the first test-tube with a second one, condense the fumes. These can be recrystallised from benzene, and then examined under the microscope, being careful to compare with a check slide of pure phthalic anhydride.

Another test devised by Storfer (*Farben Ztg.*, 1937, 42, 483), known as the resorcin test, is carried out as follows:

Two porcelain crucibles are taken. Into one place 5 c.c. of the varnish, and use the other for a blank test, both crucibles containing 1 gram of resorcin and 6 to 8 drops of H_2SO_4 . Place both crucibles in the hot-air oven and heat to 125°C . for five minutes. Take out and cool. Dissolve the contents of the respective crucibles in 25 c.c. distilled water, and make slightly alkaline with KOH solution. Should the varnish be one made with a glyptol resin a yellowish-green fluorescence should appear, indicating the presence of phthalic anhydride. The blank test shows whether the experiment was conducted correctly, and also whether the reagents used are pure.

Again, the varnish may be saponified with N/1 alcoholic KOH by refluxing for about fifteen minutes. The potassium phthalate formed is filtered off and washed four times with alcohol, and then finally identified by the resorcin test as stated above.

If, however, the potassium phthalate is weighed, a fairly approximate indication as to the amount of resin used in the original varnish can be obtained, in which case the resorcin test is omitted.

In the laboratories of the American Cyanamid and Chemical Corporation, Kappelmeier's method is used and described by Sanderson (*Paint, Oil and Chemical Review*, 1938, No. 17, 9), and is as follows: 2 to 3 grams of the sample are placed in a flask and connected with an air-cooled condenser; 10 c.c. of benzol is

then added, and when a homogeneous mixture has been obtained after carefully warming the contents of the flask, 150 c.c. N/5 alcoholic KOH is added. The whole is then refluxed for one hour and washed down with 50 c.c. ether.

The solution is then filtered and cooled through a Gooch crucible charged with a plug of paper pulp, and the potassium phthalate well washed with 200 c.c. of a mixture made of equal quantities of alcohol and benzol, being finally dried to constant weight in a vacuum desiccator; 1 gram of the potassium phthalate is equivalent to 0.5139 gram of phthalic anhydride. Provided other polybasic acids such as maleic are not present the method is excellent, but should other acids be present these will be partly precipitated as well.

Quantitative Determination of Phthalic Acid in Alkyd Resins

(K. Beneckel, *Farbe und Lack*, 1936, 451, 2).

Take 50 grams of the sample and saponify with 100 c.c. of N/2 alcoholic KOH, refluxing for six hours.

Distil off the alcohol and take up the soap residue with water. Acidify with glacial acetic acid and transfer to a separating funnel, and extract with benzene. After allowing to stand to insure complete separation, draw off the aqueous solution, which will contain the phthalic acid. Make this solution slightly alkaline, and add normal lead acetate. Allow the precipitate to settle, and then filter and wash ten times with hot water slightly acidified with acetic acid. The filter paper and precipitate are dried in an oven at 212° F. Now take the dried precipitate, and remove as much as possible to a weighed porcelain crucible. The filter paper from which practically all the precipitate has been removed is ashed in another crucible, and, when cool, transferred with a camel's-hair brush to the main precipitate, which is then fumed by adding a few drops of H_2SO_4 until all the lead has been converted to sulphate. Since one molecule of phthalic acid corresponds to one molecule of lead sulphate, the amount of phthalic acid can easily be calculated from the weight of lead sulphate. Lead phthalate ($\text{C}_6\text{H}_4(\text{CoO})_2\text{Pb}$). Another method devised by Dr. C. P. A. Kappelmeier and F. Kavanagh (*Ind. Eng. Chem.*, Ann. Edition, 1936) is carried out as follows:

Five grams of the varnish are weighed out into a 150 c.c.

Erlenmeyer flask, and add 15 to 20 c.c. N/2 alcoholic KOH. The flask is then closed with a tightly fitting rubber stopper having a wide glass tube about 3 feet high as the refluxing column, and is heated on a water bath at $40^{\circ}\text{C.} = 104^{\circ}\text{F.}$ As the saponification proceeds the potassium phthalate as a crystalline mass begins to settle out. The reaction will be finished in about two hours. The flask is then removed from the water bath, and the inside of the reflux tube and flask carefully washed out with a mixture of ether and alcohol. The ratio of alcohol to ether should be 3 in 1. The precipitate of crystals is washed into a weighed Gooch crucible containing paper pulp. Filtering should be done as rapidly as possible, as the potassium phthalate is hygroscopic, and care should be taken not to let the filter pump suck on the precipitate. Give four washes with the alcohol-ether mixture. After washing place in the oven at 100°C. for fifteen minutes, and then dry off in the desiccator under partial vacuum, then weigh to constant weight; 1 gram of potassium phthalate corresponds to 0.5760 gram of phthalic acid. The logarithmic factor is 0.76042-1, and for conversion to phthalic acid triglyceride 0.06168. The filtrate and washings in the filter flask contain the fatty acids of the alkyd varnish plus oil as potassium soaps. If these are to be determined, distil off the ether and alcohol mixture, and transfer the residue to a separating funnel, dilute with water, and acidify with N/4 HCl, using Congo red as indicator. Extract the fatty acids, after separating with ether, and wash the ether solution with a concentrated solution made with Saxa salt (NaCl) until neutral. Now filter through a fluted filter into a weighed Erlenmeyer flask and evaporate the bulk of the ether on a water bath, removing the last traces of solvent by passing in a current of dry CO_2 , and place the flask in a vacuum desiccator and finish off the drying. Weigh the residue. The residue can be qualitatively examined for china-wood oil, linseed oil, etc., and by so doing a very good idea of the varnish, etc., obtained.

Acidity.

One of the most important determinations when examining synthetic varnishes and resins is to determine the acidity. The usual and old method has a serious defect, in that it is

most difficult to tell the end point when the sample is a dark one. The method employed by the author is a modification of that known as the Albert-Coburn method, and is very satisfactory, being performed as follows:

Take 3 to 5 grams of the resin or varnish and place in a wide-mouthed boiling flask along with a mixture of 25 c.c. absolute alcohol and 25 c.c. benzene and reflux for half an hour on the water bath, then cool. Transfer the whole to a 400 c.c. Philips flask, washing the boiling flask out with alcohol and benzene mixture, transferring the washings to the Philips flask. Now add 50 c.c. neutralised solution of NaCl which has previously been cooled after being saturated with NaCl when hot, and then add 15 to 20 grams powdered Saxa salt (NaCl) and finally 20 drops of phenolphthalein. Now titrate the mixture with N/5 aqueous KOH; a perfect end point should be obtained, but it may be necessary to back-titrate once or twice with N/5 H_2SO_4 in order to obtain a sharp and clear end point. The calculation is as follows:

$$\frac{\text{C.c. of N/5 KOH taken} \times 11.2}{\text{Weight of sample}} = \text{acid value.}$$

Reactive and Non-Reactive Resins (Beck Koller and Co.).

To distinguish between these two types, melt 1 part of the resin with 3 parts ester gum. Should the mixture foam when being melted, then it is practically certain the resin is of the reactive type.

Straight Phenolics and Modified Phenolics.

In many samples the presence of phenol can be ascertained by heating the powdered resin with soda lime, when the phenol can be detected by the smell. Bradley (*Ind. Eng. Chem., Analytical Edition*, 1931, iii., 304) recommends fusing about 2 grams of the powdered resin with an equal quantity of NaOH, and after the melt has cooled extracting with 10 to 20 c.c. of boiling water and then diluting to 50 c.c., filtering and acidifying with H_2SO_4 . The liquid is then brought to the boil, when in many cases the phenol can be identified by the smell. If the phenol cannot be definitely ascertained by this means, about 1 gram of 2:6-dibromoquinone chloramide is taken and shaken

up with about 12 c.c. of distilled water, and 2 or 3 drops of the prepared reagent added to the suspected phenolic solution, which is then made alkaline with N/10 KOH, when a deep blue coloration would indicate phenol if present. As regards the presence of rosin, this can be identified in modified phenolics by the Liebermann-Storch test, or the Morini test can be carried out, and is performed as follows:

About 0.5 gram of the resin and 2.5 grams of caustic lime are slowly heated in a dry test-tube, and the fumes passed over several drops of HNO_3 having a specific gravity of 1.4. The presence of rosin is indicated by a red violet coloration, which is first violet and then greenish - blue. Shellac gives with this test very similar colour effects.

Melting Point of Resins.

There are several methods of ascertaining the melting point of synthetic resins, such as Durraus method, Nagel method and so on, but the author prefers the Paramet method as employed by the Paramet Chemical Corporation of Long Island City, U.S.A., and the following description is herewith given, which was kindly supplied by the British agents of the Corporation. In the physico-chemical sense resins have no true melting point. In all cases the fluidity of a resin increases with a rise in temperature, while the hardness decreases.

The apparatus is herewith shown, and if a number of tests are to be carried out at different temperatures it is desirable to have at least half a dozen of such apparatus. A uniform and constant heat is provided by the jacketed glass vessel (A), the inner vessel (B) being heated by the vapour of the boiling liquid in (A). By the proper choice of liquid employed—for example, butyl acetate—a great variety of temperatures can be

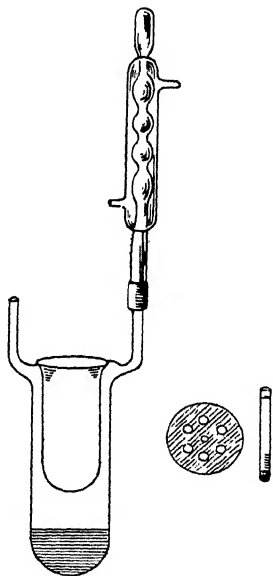


FIG. 15.

obtained. The inner vessel is covered by an asbestos plate which carries the thermometer, and six tubes which are open at both ends, being 100 mm. in length, diameter inside 8 mm., and wall thickness 1 mm., with a mark at one end 9 mm.; a cork is placed in the unmarked end, and the tubes are filled with mercury to the 9 mm. mark, and the remainder of the tube filled with resin to be tested. The resin is previously melted in a small dish, and when quite liquid run in till the tube overflows and is free from air bubbles. Now allow the tubes to cool, and then clean off any excess of resin from the sides, so that nothing remains but the solid plug of resin 9 mm. in length. The corks are then removed, and the mercury previously put in poured out. The tubes are then reversed, and to each is added 4 c.c. mercury, so that the mercury rests on the top of each plug of resin. Place the six tubes in the asbestos cover, so that a quarter of their length extends above the cover. Rubber bands are employed to keep them in position. While the tubes are being filled as previously described, the apparatus can be brought up to the constant temperature by keeping the liquid in the vessel (A) boiling. On first introducing the nest of tubes the temperature in the vessel (B) will drop, but in about twenty-five to thirty-five minutes it will be constant again. The time is noted from the moment the tubes are introduced. As the plugs of resin give way and the mercury breaks through, the time and temperature are noted; and the results reported as regards both time and temperature.

SECTION VI

USEFUL DATA

Detection of Driers in Paints (Qualitative).

Lead.

Take 20 c.c. or a sufficient amount of the sample and dilute with petroleum ether, and then shake with a solution of potassium bichromate. In the presence of lead a yellow precipitate will form at the interface between the ether layer and the aqueous layer.

Cobalt and Manganese.

A small quantity of the ether solution is shaken with dilute NaOH. On mixing the alkaline extract with benzidine in acetic acid, both manganese and cobalt will be indicated by the formation of a blue coloration. In order to distinguish between these two driers, take 20 c.c. of the paint, ash it in a silica or platinum dish, and heat the ash with dilute HNO_3 and 1 gram of red lead or lead peroxide; a purple colour will indicate manganese.

Dissolve some of the ash in dilute HCl, boil, and add potassium oxalate, and then sodium nitrite solutions; a rose-red coloration will indicate manganese. To another portion add acetic acid solution of α -nitro-beta-naphthol; a brown precipitate indicates cobalt.

Vanadium.

Dissolve some of the ashed sample in dilute HCl, add lead acetate solution. Should vanadium be present, a yellow colour due to lead vanadate, $\text{Pb}_3(\text{VO}_4)_2$, will be formed.

Rules for Converting Thermometer Scales.

- Degrees F into C. First subtract 32, then multiply by 5 and divide by 9.
 „ F „ R. First subtract 32, then multiply by 4 and divide by 9.
 „ C „ F. Multiply by 9, divide by 5, and add 32.
 „ C „ R. Multiply by 4, and divide by 5.
 „ R „ F. Multiply by 9, divide by 4, and add 32.
 „ R „ C. Multiply by 5 and divide by 4.

Thermometer Tables.

<i>Cent.</i>	<i>Réau.</i>	<i>Fahr.</i>	<i>Cent.</i>	<i>Réau.</i>	<i>Fahr.</i>	<i>Cent.</i>	<i>Réau.</i>	<i>Fahr.</i>
0	0.0	32.0	34	27.2	93.2	68	54.4	154.4
1	0.8	33.8	35	28.0	95.0	69	55.2	156.2
2	1.6	36.5	36	28.8	96.8	70	56.0	158.0
3	2.4	37.4	37	29.6	98.6	71	56.8	159.8
4	3.2	39.2	38	30.4	100.4	72	57.6	161.6
5	4.0	41.0	39	31.2	102.2	73	58.4	163.4
6	4.8	42.8	40	32.0	104.0	74	59.2	165.2
7	5.6	44.6	41	32.8	105.8	75	60.0	167.0
8	6.4	46.4	42	33.6	107.6	76	60.8	168.8
9	7.2	48.2	43	34.4	109.4	77	61.6	170.6
10	8.0	50.0	44	35.2	111.2	78	62.4	172.4
11	8.8	51.8	45	36.0	113.0	79	63.2	174.2
12	9.6	53.6	46	36.8	114.8	80	64.0	176.0
13	10.4	55.4	47	37.6	116.6	81	64.8	177.8
14	11.2	57.2	48	38.4	118.4	82	65.6	179.6
15	12.0	59.0	49	39.2	120.2	83	66.4	181.4
16	12.8	60.8	50	40.0	122.0	84	67.2	183.2
17	13.6	62.6	51	40.8	123.8	85	68.0	185.0
18	14.4	64.4	52	41.6	125.6	86	68.8	186.8
19	15.2	66.2	53	42.4	127.4	87	69.6	188.6
20	16.0	68.0	54	43.2	129.2	88	70.4	190.4
21	16.8	69.8	55	44.0	131.0	89	71.2	192.2
22	17.6	71.6	56	44.8	132.8	90	72.0	194.0
23	18.4	73.4	57	45.6	134.6	91	72.8	195.8
24	19.2	75.2	58	46.4	136.4	92	73.6	197.6
25	20.0	77.0	59	47.2	138.2	93	74.4	199.4
26	20.8	78.8	60	48.0	140.0	94	75.2	201.2
27	21.6	80.6	61	48.8	141.8	95	76.0	203.0
28	22.4	82.4	62	49.6	143.6	96	76.8	204.8
29	23.2	84.2	63	50.4	145.4	97	77.6	206.6
30	24.0	86.0	64	51.2	147.2	98	78.4	208.4
31	24.8	87.8	65	52.0	149.0	99	79.2	210.2
32	25.6	89.6	66	52.8	150.8	100	80.0	212.0
33	26.4	91.4	67	53.6	152.6			

Factors Used in Gravimetric Analysis of Pigments, Paints, and Mixed Paints.

<i>Found.</i>	<i>Sought.</i>	<i>Factor.</i>	<i>Found.</i>	<i>Sought.</i>	<i>Factor.</i>
Al ₂ O ₃	Al ₂	0.53043	CuO	Cu ₂ S	1.00040
	Al ₂ (SO ₄) ₃	3.35000	PbSO ₄	Pb	0.68293
	Sb ₂	0.78975	PbSO ₄	PbO	0.73574
	Sb ₂ O ₃	0.71424	PbSO ₄	PbCO ₃	0.88097
	Sb ₂ O ₄	0.90440	PbSO ₄	PbCrO ₄	1.06615
Mg ₂ As ₂ O ₇	As ₂	0.48274	PbSO ₄	2PbCO ₃ ·Pb(OH) ₂	0.85249
Mg ₂ As ₂ O ₇	As ₂ O ₃	0.63730	PbSO ₄	Pb	0.84056
Mg ₂ As ₂ O ₇	As ₂ O ₅	0.74034	PbCrO ₄	PbO	0.69009
As ₂ O ₃	As ₂	0.75748	PbCrO ₄	PbCO ₃	0.82632
As ₂ S ₃	As ₂	0.60918	PbCrO ₄	PbSO ₄	0.93796
As ₂ S ₃	As ₂ O ₃	0.80423	PbCrO ₄	2PbCO ₃ ·Pb(OH) ₂	0.79950
As ₂ S ₃	As ₂ O ₅	0.93425	PbO	PbSO ₄	1.35917
BaSO ₄	Ba	0.58846	PbO	2PbCO ₃ ·Pb(OH) ₂	1.15855
BaSO ₄	BaO	0.65700	PbO	Pb ₂ O ₄ (Red)	1.02393
BaSO ₄	BaCO ₃	0.84548		Lead)	
BaSO ₄	BaCl ₂	0.89226	PbO	Pb ₂ CrO ₅	1.22454
BaSO ₄	S	0.13734	PbO	PbS	1.07205
BaSO ₄	SO ₃	0.34300	PbS	PbO	0.93279
BaSO ₄	SO ₄	0.41154	2PbCO ₃ ·Pb(OH) ₂	PbO	0.86315
BaCO ₃	BaO	0.77707	2PbCO ₃ ·Pb(OH) ₂	PbCO ₃	0.68902
BaCO ₃	CO ₂	0.22290	2PbCO ₃ ·Pb(OH) ₂	Pb(OH) ₂	0.31098
CdO	Cd	0.87539	2PbCO ₃ ·Pb(OH) ₂	H ₂ O (combined)	0.02328
CdS	Cd	0.77801	Mg ₂ P ₂ O ₇	MgO	0.36190
CdS	CdO	0.88877	Mg ₂ P ₂ O ₇	MgCO ₃	0.75722
CaO	Ca	0.71464	Mn ₂ O ₄	Mn	0.72052
CaO	CaCO ₃	1.78473	Mn ₂ O ₄	MnO	0.93016
CaO	CaSO ₄	2.42804	Ni	NiO	1.27260
CaSO ₄	CaO	0.41186	NiSO ₄	NiO	0.48261
CaSO ₄	CaCO ₃	0.73505	SrCO ₃	SrO	0.70190
CaSO ₄	SO ₃	0.58814	SrSO ₄	SrO	0.56407
CO ₂	CaCO ₃	2.27430	ZnO	Zn	0.80345
CO ₂	PbO	5.06591	ZnS	ZnO	0.83514
CO ₂	MgCO ₃	1.91540	Zn ₂ P ₂ O ₇	ZnO	0.53409
Cr ₂ O ₃	Cr	0.68480	ZnS	S	0.32896
Cr ₂ O ₃	CrO ₃	1.31520	ZnSO ₄	SO ₃	0.49586
Co	CoO	1.27120	SO ₃	CaSO ₄	1.70072
CoO	Co	0.78665	SO ₃	BaSO ₄	2.91607
CoSO ₄	CoO	0.48361	SO ₃	ZnSO ₄	2.01674
Cu	CuO	1.25180	Fe	Prussian Blue	3.03000
Cu	Cu ₂ S	1.25220	N	Prussian Blue	4.40000

Factor Weights.

If the amount of material taken for analysis is that in the fourth column, each milligram of the precipitate weighed will equal the per cent. (of the substance in the first column) indicated in the last column.

<i>Substance to be Determined.</i>	<i>Precipitate weighed as :</i>	<i>Factor.</i>	<i>Weight of Sample to be Taken.</i>	<i>Each Mg. of Ppt. Represents per Cent.</i>
CaO	CaSO ₄	0.41185	0.8237	0.05
MgO	Mg ₂ P ₂ O ₇	0.36190	0.7238	0.05
Mn	Mn ₂ P ₂ O ₇	0.38722	0.7744	0.05
	Mn ₂ P ₂ O ₇	0.61256	1.2251	0.05
Pb	PbSO ₄	0.68290	0.6829	0.10
S	BaSO ₄	0.13734	1.3734	0.01
SO ₃	BaSO ₄	0.34291	1.7146	0.02
Ti	TiO ₂	0.60076	6.0076	0.01
Zn		0.36644	0.7329	0.05

To find the factor weight of any given precipitate, multiply the conversion factor as given by 0.1 and divide by the per cent. each milligram is to represent. The result will be the number of grams which should be taken for analysis.

To find the factor weight for any given volumetric solution, multiply by 100 the value of each c.c. in terms of grams of the constituent for which that solution is to be used, and divide by the per cent. each c.c. is to represent. The result will be the number of grams which should be taken for analysis.

Example.—What weight of iron oxide must be taken in order that each c.c. of a permanganate solution may represent 1 per cent. of metallic iron in the sample ?

The strength of the permanganate is 1 c.c. = 0.0065 gram of iron; therefore the proper amount of sample to take for the

determination is $\frac{0.0065 \times 100}{1.0} = 0.6500$ gram.

Volumetric Analysis.*Standard Solutions.*

<i>Standard Solutions.</i>	<i>Grams per Litre.</i>
Normal hydrochloric acid, HCl	36.5
Normal sulphuric acid, H ₂ SO ₄	49
Normal caustic soda, NaOH	40
Normal caustic potash, KOH	56
Normal sodium carbonate, Na ₂ CO ₃	53
Normal potassium iodide, KI	166
Normal oxalic acid, COOH.COOH	63.024
Semi-normal potassium ferrocyanide, K ₄ Fe(CN) ₆ .3H ₂ O	52.75
Semi-normal potassium cyanide, KCN	32.50
Semi-normal arsenious oxide, As ₂ O ₃	49.50
Decinormal potassium dichromate, K ₂ Cr ₂ O ₇	4.9133
Decinormal potassium permanganate, KMnO ₄	3.156
Decinormal sodium thiosulphate, Na ₂ S ₂ O ₃ .5H ₂ O	24.827
Decinormal iodine, I ₂ (18 grams KI)	12.7
Decinormal silver nitrate, AgNO ₃	16.966
Decinormal ammonium sodium phosphate, NaNH ₄ HPO ₄ .4H ₂ O	20.9

The following example will illustrate standardisation: Sulphuric acid should contain 49 grams of the anhydrous acid per 1,000 c.c. Dilute about 40 c.c. of pure sulphuric acid to, say, 1,250 c.c.; when quite cold, determine the strength by titration with a normal alkali solution. Dilute the sulphuric acid so that 1 c.c. shall exactly neutralise 1 c.c. of normal alkali. The number of c.c. of distilled water that is required to be added to 1 litre of the acid solution in order to make it of the correct strength can be found by the following formula:

$\frac{b}{a} = 1$) $\times 1,000$, where b c.c. of normal alkali are required to neutralise a c.c. of sulphuric acid. After the dilution, check up the strength again with normal alkali.

Some Volumetric Methods.*Aluminium.*

The aluminium present can be estimated by mixing with excess of sodium acetate, and then adding an excess of N/10 ammonium sodium phosphate. Heat to boiling, and titrate

the excess of phosphate with standard (20.9 grams per 1,000 c.c.) uranium acetate solution. The indicator used is freshly prepared potassium ferrocyanide solution 10 per cent. strength (35 grams per 1,000 c.c.). 1 c.c. N/10 ammonium-sodium phosphate = 0.00513 gram Al_2O_3 .

Antimony.

The tartrate solution is neutralised with Na_2CO_3 ; then add excess of NaHCO_3 and titrate with N/10 iodine. 1 c.c. = 0.006 gram Sb.

Barium.

Titrate with a standard solution of potassium dichromate (7.37 grams per 1,000 c.c.) in an ammoniacal solution at 65° C. until the supernatant solution is a pale yellow. 1 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ = 0.00684 Ba.

Calcium.

Having obtained the calcium oxalate, dissolve in dilute H_2SO_4 and make up to 300 c.c. and titrate with N/10 potassium permanganate. 1 c.c. = 0.0028 gram CaO.

Chromium.

To the chromium solution add an excess of iron alum (ammonium ferrous sulphate) and titrate with N/10 potassium dichromate. 1 c.c. = $\text{Fe} \times 0.3119 = \text{Cr}$.

Iron.

Titrate with N/10 potassium dichromate in the presence of chlorides, first reducing with a solution of stannous chloride and then getting rid of the excess with a few drops of mercuric chloride. 1 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ = 0.00798 Fe_2O_3 .

Lead.

Precipitate as chromate. Wash and dissolve in special solution $\text{NaCl} + \text{HCl}$ (NaCl 550 grams, HCl 250 c.c., distilled water 2,000 c.c.), add KI, and titrate with N/10 sodium thiosulphate, using starch solution as indicator. 1 c.c. $\text{Na}_2\text{S}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ = 0.007433 PbO.

Manganese.

Take the HCl solution, add bromine in the presence of a ferric salt, and precipitate the manganese. Dissolve in HNO_3 , evaporate off the excess acid, neutralise with an emulsion of ZnO, and titrate with N/10 potassium permanganate to a faint pink. $1 \text{ c.c.} = \text{Fe} \times 0.491 = \text{Mn}$ or $\text{Fe} \times 0.7768 = \text{MnO}_2$.

Zinc.

Potassium ferrocyanide solution 41.25 grams per 1,000 c.c.
 $1 \text{ c.c.} = 0.01 \text{ gram zinc.}$

Factors for use in Volumetric Analysis.

			<i>Grams per Litre.</i>
Normal sulphuric acid			.. 49.043
Normal hydrochloric acid			.. 36.468
Normal oxalic acid 63.024
Na, 0.02300	K, 0.03910	Ca, 0.02004	
Na_2O , 0.03100	K_2O , 0.04710	CaO , 0.02804	
NaOH , 0.04001	KOH , 0.05611	Ca(OH)_2 , 0.03705	
Na_2CO_3 , 0.05300	K_2CO_3 , 0.06910	CaCO_3 , 0.05004	
NaHCO_3 , 0.08401	KHCO_3 , 0.10011	NH_3 , 0.01703	

Normal sodium hydrate: 40.008 grams per litre.

H_2SO_4 , 0.04904	HI , 0.12793
SO_3 , 0.04003	$\text{HC}_2\text{H}_3\text{O}_2$, 0.06003
HCl , 0.03647	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 0.06302
HNO_3 , 0.06302	$\text{H}_2\text{C}_2\text{O}_4$ (anhydrous), 0.04501
HBr , 0.08093	$\text{HC}_{18}\text{H}_{33}\text{O}_2$ (oleic), 0.28227

Decinormal silver nitrate: 16.989 grams per litre.

NaCl , 0.005846	NH_4Cl , 0.00535
NaBr , 0.01029	NH_4Br , 0.00980
KCl , 0.00746	Cl , 0.003546
KBr , 0.01190	Br , 0.00799
KCN , 0.01302	I , 0.01269

Decinormal sodium chloride: 5.846 grams per litre.

AgNO_3 , 0.01699

Decinormal potassium dichromate: 4.9033 grams per litre.

Fe , 0.00558	Cr_2O_3 , 0.00253
FeO , 0.00718	Mn , 0.00275
Fe_2O_3 , 0.00798	MnO , 0.00355
Cr , 0.00173	MnO_2 , 0.00435

Decinormal potassium permanganate: 3.1606 grams per litre.

Fe, 0.005585	CaO, 0.00280
FeO, 0.007185	Cd, 0.00140
FeCO ₃ , 0.011585	CdO, 0.00160
FeSO ₄ , 0.015192	Cr, 0.00173
Sb, 0.00601	Cr ₂ O ₃ , 0.00253

Decinormal iodine: 12.692 grams per litre.

As, 0.00375	NaHSO ₄ , 0.00520
As ₂ O ₃ , 0.00495	KHSO ₄ , 0.00601
Cd, 0.00562	Ca(HSO ₃) ₂ , 0.00506
CdS, 0.00642	Na ₂ S ₂ O ₃ ·5H ₂ O, 0.02482
SO ₂ , 0.00320	Sn, 0.00594

Decinormal sodium thiosulphate: 24.822 grams per litre.

Cu, 0.006357	S, 0.001067
Pb, 0.006900	MnO ₂ , 0.00435
PbO, 0.007433	Cl, 0.003546
Ba, 0.004577	I, 0.01269

Standard ferrous sulphate solution:

Ferrous ammonium sulphate	..	84 grams.
Sulphuric acid	200 c.c.
Distilled water to	1,000 c.c.

1 c.c.=approximately 12 mgm. of Fe.

Reactions involved in Volumetric Analysis.

Antimony : $5\text{Sb}_2\text{O}_3 + 4\text{KMnO}_4 = 5\text{Sb}_2\text{O}_5 + \text{K}_2\text{O} + 4\text{MnO}$.

Arsenic : (i) $\text{As}_2\text{O}_3 + \text{I}_2 + 3\text{H}_2\text{O} = \text{As}_2\text{O}_5 + 4\text{HI}$.

(ii) $\text{H}_3\text{AsO}_4 + (\text{UO}_2)(\text{C}_2\text{H}_3\text{O}_2)_2 = (\text{UO}_2)\text{HAsO}_4$

Barium : $2\text{BaCrO}_4 + 6\text{KI} = \text{Cr}_2\text{O}_3 + 3\text{K}_2\text{O} + 3\text{I}_2$
and $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$.

Cadmium : (i) $8\text{KMnO}_4 + 5\text{CdS} + 24\text{HCl} =$
 $8\text{KCl} + 8\text{MnCl}_2 + 5\text{CdSO}_4 + 12\text{H}_2\text{O}$.

(ii) $\text{CdS} + 2\text{HCl} + \text{I}_2 = \text{CdCl}_2 + 2\text{HI} + \text{S}$.

Calcium : $5\text{Ca}(\text{COO})_2 + 2\text{KMnO}_4 = \text{K}_2\text{O} + 2\text{MnO} + 10\text{CO}_2 + 5\text{CaO}$.

Chromium : $2\text{CrO}_3 + 6\text{FeO} = 3\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$.

Iron : (i) $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{FeO} = 3\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Cr}_2\text{O}_3$.

(ii)

Lead : (i) $(\text{CH}_3\text{COO})_2\text{Pb} + (\text{NH}_4)_2\text{MoO}_4 = \text{PbMoO}_4 + 2(\text{CH}_3\text{COO})\text{NH}_4$.

(ii) $2\text{PbCrO}_4 + 6\text{KI} = \text{Cr}_2\text{O}_3 + 3\text{K}_2\text{O} + 3\text{I}_2$
and $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$.

Manganese : (i) $\text{MnO}(\text{OH})_2 + (\text{COOH})_2 = \text{MnO} + 2\text{CO}_2 + 2\text{H}_2\text{O}$.

(ii) $3\text{MnO} + 2\text{KMnO}_4 = 5\text{MnO}_2 + \text{K}_2\text{O}$.

Tin : $\text{SnCl}_2 + 2\text{HCl} + \text{I}_2 = \text{SnCl}_4 + 2\text{HI}$.

Zinc : $\text{K}_4\text{Fe}(\text{CN})_6 + 2\text{ZnCl}_2 = \text{Zn}_2\text{Fe}(\text{CN})_6 + 4\text{KCl}$
and $3\text{Zn}_2\text{Fe}(\text{CN})_6 + \text{K}_4\text{Fe}(\text{CN})_6 = 2\text{K}_2\text{Zn}_3(\text{Fe}(\text{CN})_6)_2$.

Indicators.

Cochineal.—Digest 1 gram of crushed cochineal in 100 c.c. of 25 per cent. alcohol and filter.

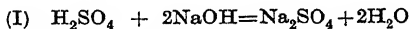
Methyl Orange.—Dissolve 0.1 gram in 100 c.c. of distilled water.

Phenolphthalein.—Dissolve 1 gram in 100 c.c. of 50 per cent. alcohol.

Lacmoid.—Dissolve 0.2 gram in 100 c.c. of 50 per cent. alcohol.

Rosolic Acid.—Dissolve 0.5 gram in 50 per cent. alcohol.

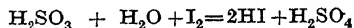
When possible, volumetric methods should be used, as by so doing a considerable saving of time is effected when conducting daily a large number of routine tests. For the benefit of students, in order that they may more fully understand the measuring of a volumetric solution, the following examples are given:



$$\begin{array}{r} 2)97.34 \\ \hline 48.67 \end{array} \quad \begin{array}{r} 2)79.52 \\ \hline 39.76 \end{array}$$

48.67 39.76 = grams in 1,000 c.c. normal solution.

(II) Sulphurous acid (SO_2 determination):

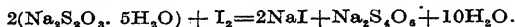


$$\begin{array}{r} 20)81.46 \\ \hline 4.073 \end{array} \quad \begin{array}{r} 20)251.8 \\ \hline 12.59 \end{array}$$

4.073

12.59 = grams in 1,000 c.c. N/10 solution.

Sodium Thiosulphate :



20)492.88

20)251.8

24.644

12.59=grams in 1,000 c.c. of N/10 solution.

Hydrometers.

Conversion of specific gravity into Twaddell (tw.):

Multiply by 1,000, subtract 1,000, and divide by 5.

Example: Convert 1.160 specific gravity to degrees Twaddell—

$$\begin{array}{r} 1.160 \times 1,000 = 1,160 \\ 1,000 \end{array}$$

$$5)160 = 32 \text{ tw.}$$

Conversion of Twaddell to specific gravity:

Multiply by 5, add 1,000, and divide by 1,000.

Example: Convert 40 Twaddell to specific gravity—

$$\begin{array}{r} 40 \times 5 = 200 \\ \text{add } 1,000 \end{array}$$

$$1,200$$

$$\text{divide by } 1,000 = 1.200 \text{ specific gravity.}$$

Baumé scale (rational) at 15° C.:

$$\frac{144.3}{144.3 - \text{reading of hydrometer.}}$$

$$144.3 - \text{reading of hydrometer.}$$

Hydrometer Conversion Table.

Conversion of degrees Baumé (rational scale) and Twaddell to specific gravity at 15° C.:

Baumé (Rat'nal).	Twad- dell.	Specific Gravity at 15° C.	Baumé (Rat'nal).	Twad- dell.	Specific Gravity at 15° C.	Baumé (Rat'nal).	Twad- dell.	Specific Gravity at 15° C.
0	0	1.000	23	38.0	1.190	46	93.6	1.468
1	1.4	1.007	24	40.0	1.200	47	96.6	1.483
2	2.8	1.014	25	42.0	1.210	48	99.6	1.498
3	4.4	1.022	26	44.0	1.220	49	103.0	1.515
4	5.8	1.029	27	46.2	1.231	50	106.0	1.530
5	7.4	1.037	28	48.2	1.241	51	109.2	1.546
6	9.0	1.045	29	50.4	1.252	52	112.6	1.563
7	10.2	1.052	30	52.6	1.263	53	116.0	1.580
8	12.0	1.060	31	54.8	1.274	54	119.4	1.597
9	13.4	1.067	32	57.0	1.285	55	123.0	1.615
10	15.0	1.075	33	59.4	1.297	56	127.0	1.635
11	16.6	1.083	34	61.6	1.308	57	130.4	1.652
12	18.2	1.091	35	64.0	1.320	58	134.2	1.671
13	20.0	1.100	36	66.4	1.332	59	138.2	1.691
14	21.6	1.108	37	69.0	1.345	60	142.0	1.710
15	23.2	1.116	38	71.4	1.357	61	146.4	1.732
16	25.0	1.125	39	74.0	1.370	62	150.6	1.753
17	26.8	1.134	40	76.6	1.383	63	155.0	1.775
18	28.4	1.142	41	79.4	1.397	64	159.0	1.795
19	30.4	1.152	42	82.0	1.410	65	164.0	1.820
20	32.4	1.162	43	84.8	1.424	66	168.4	1.842
21	34.2	1.171	44	87.6	1.438	67	173.0	1.865
22	36.0	1.180	45	90.6	1.453			

Mensuration Formulæ.

Square.—Area=(side)².

Cube or Rectangular Vessel.—Volume=length × breadth × height.

Triangle.—Area= $\frac{1}{2}$ base × perpendicular height.

Circle.—Area=3.1416 × (radius)².

Circumference=3.1416 × diameter.

Ellipse.—Area=0.7854 × long axis × short axis.

Sphere.—Surface=3.1416 × (diameter)².

Volume= $\frac{4}{3}$ × 3.1416 × (radius)³.

Cylinder or Prism.—Volume=area of base × height.

Surface=area of both ends + (length × perimeter).

Cone or Pyramid.—Volume= $\frac{1}{3}$ × area of base × perpendicular height.

Surface=area of base + (perimeter × $\frac{1}{2}$ slant height).

Cask or Barrel.—Volume=0.2618 L (2D² + d²) cub. ins.

=0.0009425 L (2D² + d²) gallons.

Where L=length in inches.

D=internal diameter in inches at the widest part.

d=internal diameter in inches at the ends.

Weight and Volume Equivalents.

1 lb.=953.6 grams.	1 pint=1½ lbs.
1 ounce=28.35 grams.	1 quart=2½ lbs.
1 gram=15.43 grains.	1 gallon=4 quarts.
1 grain=0.0645 gram.	1 gallon=10 lbs.
1 kilogram=35.27 ounces.	1 gallon=4.5 litres.
1 kilogram=2.2 lbs.	1 stone (14 lbs.)=6.35 kilograms.
1 litre=0.22 gallon.	1 quarter (28 lbs.)=12.7 kilograms.
1 litre=1.76 pints.	1 cwt. (112 lbs.)=50.8 kilograms.
1 litre=35.2 fluid ounces.	1 ton (20 cwt.)=1016.0 kilograms.
1 fluid ounce=28.4 c.c.	85 minims=5 c.c. (1 teaspoonful).
1 pint=568 c.c.	255 minims=15 c.c. (1 tablespoonful).
1 pint=20 fluid ounces.	

Table for Converting English Weights into Metric Weights.

	<i>Grams.</i>	<i>Lbs.</i>		<i>Grams.</i>	<i>Qr.</i>		<i>Grams.</i>	
$\frac{1}{4}$	=	7.09	4	=	1814.4	1	=	12700.5
$\frac{1}{2}$	=	14.17	5	=	2268.0	2	=	25401.0
$\frac{3}{4}$	=	21.26	6	=	2721.6	3	=	38101.5
1	=	28.35	7	=	3175.2	4	=	50802.0
2	=	56.70	8	=	3628.8	<i>Cwts.</i>	<i>Kilos.</i>	
3	=	85.05	9	=	4082.4	1	=	50.8
4	=	113.40	10	=	4535.9	2	=	101.6
5	=	141.75	11	=	4989.6	3	=	152.4
6	=	170.10	12	=	5443.2	4	=	203.2
7	=	198.44	13	=	5896.8	5	=	254.0
8	=	226.79	14	=	6350.4	6	=	304.8
9	=	255.14	15	=	6804.0	7	=	355.6
10	=	283.49	16	=	7257.6	8	=	406.4
11	=	311.84	17	=	7711.2	9	=	457.2
12	=	340.19	18	=	8164.6	10	=	508.0
13	=	368.54	19	=	8618.4	11	=	558.8
14	=	396.89	20	=	9072.0	12	=	609.6
15	=	425.24	21	=	9525.6	13	=	660.4
16	=	453.59	22	=	9979.2	14	=	711.2
			23	=	10432.8	15	=	762.0
			24	=	10886.4	16	=	812.8
<i>Lbs.</i>	<i>Grams.</i>		25	=	11340.0	17	=	863.6
1	=	453.59	26	=	11793.6	18	=	914.4
2	=	907.18	27	=	12247.2	19	=	965.2
3	=	1360.8	28	=	12700.5	20	=	1016.0

1,000 grams equals 1 kilogram.

International Atomic Weights (1941).

<i>Element.</i>	<i>Symbol.</i>	<i>Atomic Weight.</i>	<i>Element.</i>	<i>Symbol.</i>	<i>Atomic Weight.</i>
Aluminium ..	Al	26.97	Neon ..	Ne	20.183
Antimony ..	Sb	121.76	Nickel ..	Ni	58.69
Argon ..	A	39.944	Niobium (Colum- bium) ..	Nb(Cb)	92.91
Arsenic ..	As	74.91	Nitrogen ..	N	14.008
Barium ..	Ba	137.36	Osmium ..	Os	190.2
Beryllium ..	Be	9.02	Oxygen ..	O	16.0000
Bismuth ..	Bi	209.00	Palladium ..	Pd	106.7
Boron ..	B	10.82	Phosphorus ..	P	30.98
Bromine ..	Br	79.916	Platinum ..	Pt	195.23
Cadmium ..	Cd	112.41	Potassium ..	K	39.098
Cesium ..	Cs	132.91	Praseodymium ..	Pr	140.92
Calcium ..	Ca	40.08	Protoactinium ..	Pa	231
Carbon ..	C	12.010	Radium ..	Ra	226.05
Cerium ..	Ce	140.13	Radon ..	Rn	222
Chlorine ..	Cl	35.457	Rhenium ..	Re	186.31
Chromium ..	Cr	52.01	Rhodium ..	Rh	102.91
Cobalt ..	Co	58.94	Rubidium ..	Rb	85.48
Copper ..	Cu	63.57	Ruthenium ..	Ru	101.7
Dysprosium ..	Dy	162.46	Samarium ..	Sm	150.43
Erbium ..	Er	167.2	Scandium ..	Sc	45.10
Europium ..	Eu	152.0	Selenium ..	Se	78.96
Fluorine ..	F	19.00	Silicon ..	Si	28.06
Gadolinium ..	Gd	156.9	Silver ..	Ag	107.880
Gallium ..	Ga	69.72	Sodium ..	Na	22.997
Germanium ..	Ge	72.60	Strontium ..	Sr	87.63
Gold ..	Au	197.2	Sulphur ..	S	32.06
Hafnium ..	Hf	178.6	Tantalum ..	Ta	180.88
Helium ..	He	4.003	Tellurium ..	Te	127.61
Holmium ..	Ho	164.94	Terbium ..	Tb	159.2
Hydrogen ..	H	1.008	Thallium ..	Tl	204.39
Indium ..	In	114.76	Thorium ..	Th	232.12
Iodine ..	I	126.92	Thulium ..	Tm	169.4
Iridium ..	Ir	193.1	Tin ..	Sn	118.70
Iron ..	Fe	55.85	Titanium ..	Ti	47.90
Krypton ..	Kr	83.7	Tungsten ..	W	183.92
Lanthanum ..	La	138.92	Uranium ..	U	238.07
Lead ..	Pb	207.21	Vanadium ..	V	50.95
Lithium ..	Li	6.940	Xenon ..	Xe	131.3
Lutecium ..	Lu	174.99	Ytterbium ..	Yb	173.04
Magnesium ..	Mg	24.32	Yttrium ..	Yt	88.92
Manganese ..	Mn	54.93	Zinc ..	Zn	65.38
Mercury ..	Hg	200.61	Zirconium ..	Zr	91.22
Molybdenum ..	Mo	95.95			
Neodymium ..	Nd	144.27			

Percentages Converted to English Weights.

Per Cent.	For 100 lbs.			For 75 lbs.			For 50 lbs.			For 25 lbs.			For 10 lbs.		
	ozs.	drs.	grs.	ozs.	drs.	grs.	ozs.	drs.	grs.	ozs.	drs.	grs.	ozs.	drs.	grs.
1 ..	16			12			8			4			1	9	16
0.9 ..	14	6		10	8		7			3	8		1	7	5
0.8 ..	12	12	14	9	9	10	6	6	7	3	3	3	1	4	12
0.75 ..	12			9			6			3			1	3	5
0.7 ..	11	3		8	6	7	5	9	14	2	12	21	1	1	25
0.6 ..	9	9	11	7	3		4	12	19	2	6	9		15	9
0.5 ..	8			6			4			2				12	22
0.4 ..	6	6		4	12	14	3	3		1	9	14		10	10
0.3 ..	4	12	14	3	9	10	2	6	7	1	3	3		7	18
0.25 ..	4			3	0	0	2			1				6	11
0.2 ..	3	2	20	2	6	1	1	9	10		12	19		5	
0.1 ..	1	9	10	1	3			12	19		6	9		2	
0.09 ..	1	6	14	1	0	24		11	7		5	17		2	7
0.08 ..	1	4	0		15			10			5			2	
0.075 ..	1	2	21		14	1		9	10		4	19		1	24
0.07 ..	1	1	14		13	3		8	21		4	10		1	21
0.06 ..		15			11	7		7	14		3	21		1	14
0.05 ..		12	14		9	10		6	7		3	3		1	7
0.04 ..		10			7	14		5			2	14		1	
0.03 ..		7	14		5	17		3	21		1	24			
0.025 ..		6	7		4	18		3	3		1	15			
0.02 ..		5			3	21		2	14		1	7			
0.01 ..		2	14		1	24		1	7						
0.009 ..		2	7		1	18		1	3						
0.008 ..		2			1	14		1							
0.0075 ..		1	24		1	11									
0.007 ..		1	21		1	8									
0.006 ..		1	14		1	3									
0.005 ..		1	7												
0.004 ..		1													

Example.—To convert 0.08 per cent. on 35 lbs. into English weight:

0.08 per cent. for 25 lbs.=5 drms.

0.08 per cent. for 10 lbs.=2 drms.

Therefore 0.08 per cent. for 35 lbs.=7 drms.

Equivalents in Metric and U.S. Systems of Measures.

Cubic centimetre	0.061 cubic inch.
Cubic inch ..	16.39 cubic centimetres.
Millimetre ..	0.0338 U.S. liquid ounce.
U.S. liquid ounce	29.57 millilitres.
Litre	1.057 U.S. liquid quart.
U.S. liquid quart	0.946 litres.
Litre	0.2642 U.S. liquid gallon.
U.S. liquid gallon	3.785 litres.
Gram	0.0353 avoirdupois ounce.
Avoirdupois ounce	28.35 grams.
Gram	0.002205 avoirdupois pound.
Avoirdupois pound	453.6 grams.
Kilo	2.205 avoirdupois pounds.
Avoirdupois pound	0.4536 kilo.
Metric ton ..	1.102 short ton (2,000 lbs.).
Short ton ..	0.907 metric ton.

Terms used in Connection with Paints and Varnish.

Abrasive Resistance.—This property is comparable with toughness rather than hardness. It is that property exhibited by the surface of a paint, enamel, or varnish which will resist being worn away by rubbing or friction.

Acicular.—Refers to pigment particles which are needle-shaped, and is especially used in the case of certain types of zinc oxide.

Actinic Rays.—The rays of light which produce chemical change situated in the blue and ultra-violet range of the spectrum.

Adsorption.—Not to be confused with absorption; adsorption is akin to adhesion, and is that property which brings about an accumulation or increase of molecules from one medium which is in contact with another to such adjacent surface.

Aligating.—A type of paint coat failure due to cracks forming on the surface coat. Sometimes due to applying paint to unseasoned wood and at others to a coat of paint being applied to an undercoat which is relatively soft, hence all undercoats are much improved by the addition of zinc oxide.

Bleeding.—When a pigment or dye in a previous coat comes through the top coat. This usually occurs when using a lake type of pigment which is soluble in the medium of the newly applied top coat.

Blushing.—This term is usually applied to lacquers when they become or show an opaque appearance, which may be due to the solid constituents becoming partly or entirely precipitated due to condensed moisture, or it may be brought about by improper solvent balance.

Brittleness.—This is the opposite to toughness or tenacity. In a varnish this phenomenon is exhibited by the film cracking and flaking when bent. The kauri reduction test is frequently used to determine the degree of brittleness.

Chalking.—A phenomenon of paint coats shown by the presence of loose powder on the film of paint or just beneath the surface, detected by rubbing the film with a piece of black velvet in the case of white paints.

Checking.—A phenomenon exhibited by coating of paint, enamel, etc., by slight breaks on the surface. These breaks are known as checks when an underlying coat is visible. There are two types, macroscopic and microscopic. The former can be seen with the naked eye, the latter require a magnifying lens to see them.

Dulling.—An expression used to describe loss of gloss which develops in a varnish film after it has dried out. It may be due to the action of gases or to defective cooking of the varnish.

Elastic Limit.—A maximum stress of stretching which a film will withstand, and is still capable of regaining its original length after the force has been removed.

False Body.—An abnormal increase in consistency which gives the impression that, on drying, the paint will exhibit a thick film, whereas the reverse may be true.

Feeding.—As applied to varnishes, is frequently due to over-polymerisation. The feeding up or livering of basic pigments is due to the excessive formation of soaps brought about by a too high acid value of the oil or varnish used. Moisture also in the pigment may be responsible for feeding or livering up. The final stages of livering results in a coagulated mass.

Mobility.—Mobility, in other words fluidity, can be defined as the ease with which the material flows; in other words, the greater the mobility, the less the viscosity.

Plasticity.—A property of solids by virtue of which they keep their shape permanently under the action of a small shearing stress, but would become deformed under greater pressure.

Thixotropy.—A change in consistency of a paint which takes place when it is allowed to remain in an undisturbed condition; when the paint increases in body the change is called positive thixotropy, but when it decreases it is known as negative thixotropy. Some assume that thixotropy and gel structure are related.

The Chemical Names and Formulæ of Common Chemicals and Pigments.

<i>Common Name.</i>	<i>Chemical Name.</i>	<i>Formula.</i>
Acid of Sugar	Oxalic acid	$C_2H_2O_4$
Alum Cake	Aluminium sulphate	$Al_2(SO_4)_3 \cdot 9H_2O$
Alumina	Aluminium oxide	Al_2O_3
Antimony Black	Antimony trisulphide	Sb_2S_3
Antimony Vermilion	Antimony oxysulphide	$Sb_2S_3 \cdot Sb_2O_3$
Antimony White	Antimonious oxide	Sb_2O_3
Aqua Fortis	Nitric acid	HNO_3
Aqua Regia	Nitric acid + Hydrochloric acid	$HNO_3 + 3HCl$
Barium White	Barium sulphate	$BaSO_4$
Barytes	Barium sulphate	$BaSO_4$
Bichrome	Potassium bichromate	$K_2Cr_2O_7$
Blanc Fixe	Barium sulphate	$BaSO_4$
Bleaching Powder	Calcium chloro - hypo - chlorite	$CaOCl_2$
Blue Salts	Nickel sulphate	$NiSO_4 \cdot 7H_2O$
Bluestone	Copper sulphate	$CuSO_4 \cdot 5H_2O$
Blue Verditer	Basic copper carbonate	$2CuCO_3 \cdot Cu(OH)_2$
Blue Vitriol	Copper sulphate	$CuSO_4 \cdot 5H_2O$
Borax	Sodium tetraborate	$Na_2B_4O_7 \cdot 10H_2O$
Bremen Blue	Basic copper carbonate	$xCuCO_3 \cdot yCu(OH)_2$
Brimstone	Sulphur	S
Burnt Lime	Calcium oxide	CaO
Burnt Ochre	Ferric oxide	Fe_2O_3
Butter of Antimony	Antimony trichloride	$SbCl_3$
Cadmium Yellow	Cadmium sulphide	CdS
Calamine	Zinc carbonate	$ZnCO_3$

<i>Common Name.</i>	<i>Chemical Name.</i>	<i>Formula.</i>
Calcite	Mineral calcium carbonate	CaCO_3
Calomel	Mercurous chloride	Hg_2Cl_2
Caustic Potash	Potassium hydroxide	KOH
Caustic Soda	Sodium hydroxide	NaOH
Chalk	Calcium carbonate	CaCO_3
China Clay	Aluminium silicate	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Chinese Red	Basic lead chromate	$\text{PbCrO}_4 \cdot \text{PbO}$
Chinese White	Zinc oxide	ZnO
Chrome Green	Chromium oxide	Cr_2O_3
Chrome Red	Basic lead chromate	$\text{PbCrO}_4 \cdot \text{PbO}$
Chrome Yellow	Lead chromate	PbCrO_4
Cobalt Black	Cobalt oxide	CoO
Cobalt Green	Cobalt zincate	$\text{CoO} \cdot \text{ZnO}$
Copperas	Ferrous sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Corrosive Sublimate	Mercuric chloride	HgCl_2
Derby Red	Basic lead chromate	$\text{PbCrO}_4 \cdot \text{PbO}$
Emerald Green	Copper aceto-arsenite	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{CuAs}$
Epsom Salts	Magnesium sulphate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Ferro-prussiate	Potassium ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$
Fixed White	Barium sulphate	BaSO_4
French Chalk	Hydrated silicate of magnesium	$\text{Mg}_3\text{Si}_4\text{O}_{11} \cdot \text{H}_2\text{O}$
French Verdigris	Basic copper acetate	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{CuO} +$
Glauber's Salts	Sodium sulphate	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Green Verditer	Basic copper carbonate	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
Green Vitriol	Ferrous sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Gypsum	Calcium sulphate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Heavy Spar	Barium sulphate	BaSO_4
Horn Silver	Silver chloride	AgCl
Hypo	Sodium thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
Indian Red	Ferric oxide	Fe_2O_3
Iron Black	Precipitated antimony	Sb
Kaolin	Aluminium silicate	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Kieselguhr	Silicious earth	SiO_2
King's Yellow	Arsenic sulphide	As_2S_3
Litharge	Lead monoxide	PbO
Lithopone	Zinc sulphide + Barium sulphate	$\text{ZnS} + \text{BaSO}_4$
Lunar Caustic	Silver nitrate	AgNO_3
Magnesia	Magnesium oxide	MgO
Malachite	Basic copper carbonate	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
Manganese Black	Manganese dioxide	MnO_2
Marble	Calcium carbonate	CaCO_3
Massicot	Lead monoxide	PbO
Milk of Barium	Barium hydroxide	$\text{Ba}(\text{OH})_2$
Milk of Lime	Calcium hydroxide	$\text{Ca}(\text{OH})_2$

<i>Common Name.</i>	<i>Chemical Name.</i>	<i>Formula.</i>
Milk of Magnesia	Magnesium hydroxide	$\text{Mg}(\text{OH})_2$
Minium	Lead tetroxide	Pb_3O_4
Muriatic acid	Hydrochloric acid	HCl
Orpiment	Arsenic trisulphide	As_2S_3
Paris Blue	Ferric ferrocyanide	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
Paris Green	Copper aceto-arsenite	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{CuAs}_2\text{O}_7$
Pearl Ash	Potassium carbonate	K_2CO_3
Permanent White	Barium sulphate	BaSO_4
Plaster of Paris	Calcium sulphate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Precipitated Chalk	Calcium carbonate	CaCO_3
Prussian Blue	Ferric ferrocyanide	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
Putty Powder	Impure stannic oxide	SnO_2
Realgar	Arsenic disulphide	As_2S_2
Red Antimony	Antimony oxysulphide	$\text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$
Red Lead	Lead tetroxide	Pb_3O_4
Red Precipitate	Oxide of mercury	HgO
Red Prussiate of Potash	Potassium ferricyanide	$\text{K}_3\text{Fe}(\text{CN})_6$
Rouge	Ferric oxide	Fe_2O_3
Salt of Lemon	Potassium hydrogen oxalate	$\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Salt of Sorrel	Potassium hydrogen oxalate	$\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Salt of Tartar	Potassium carbonate	K_2CO_3
Satin White	Calcium sulphate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Scheele's Green	Copper hydrogen arsenite	CuHAsO_3
Soda Crystals	Sodium carbonate	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Soluble Glass	Sodium silicate	Na_2SiO_3
Spirits of Hartshorn	Ammonia	NH_4OH
Sugar of Lead	Lead acetate	$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$
Talc	Hydrated magnesium silicate	$\text{Mg}_3\text{Si}_4\text{O}_{11} \cdot \text{H}_2\text{O}$
Tartar Emetic	Potassium antimony tartrate	$\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$
Tin Crystals	Stannous chloride	SnCl_2
Tin Salt	Stannous chloride	SnCl_2
Tin White	Stannic hydroxide	$\text{Sn}(\text{OH})_4$
Turnbull's Blue	Ferrous ferricyanide	$\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
Ultramarine yellow	Barium chromate	BaCrO_4
Venetian Red	Ferric oxide	Fe_2O_3
Verdigris	Basic copper acetate	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{CuO} + 6\text{H}_2\text{O}$
Vermilion	Red mercuric sulphide	HgS
Vinegar Salts	Calcium acetate	$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$
Vitriol	Sulphuric acid	H_2SO_4
Washing Soda	Sodium carbonate	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
White Arsenic	Arsenious oxide	As_2O_3
White Lead	Basic lead carbonate	$2\text{PbCO}_3 + \text{Pb}(\text{OH})_2$

<i>Common Name.</i>	<i>Chemical Name.</i>	<i>Formula.</i>
White Vitriol	Zinc sulphate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Whiting	Calcium carbonate	CaCO_3
Yellow Prussiate of Potash	Potassium ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$
Zinc Vitriol	Zinc sulphate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Zinc White	Zinc oxide	ZnO

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